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Keynote Speakers

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Challenges in zeolite synthesis for catalytic applications

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The name zeolites, coined in 1756 and meaning 'boiling stones', refers to a diverse but uniform class of natural and synthetic crystalline aluminosilicates and related compositions with framework structures containing well-defined micropores, which can adsorb and discriminate molecules based on their size and shape. Zeolites are widely used in petroleum and chemical industries because of exceptional catalytic and selective adsorption properties in combination with thermal and chemical stability as well as environmental friendliness. Zeolites crystallize readily and spontaneously under hydrothermal conditions from suitably adjusted synthesis mixtures. There is a continuous ongoing effort to discover new framework structures, to expand and improve applications and to gain better fundamental understanding, which is now primarily empirical. The traditional zeolites have been conceptualized as 3D networks but a recent breakthrough revealed their formation as crystalline layered solids,[1] which has had far reaching implications, e.g. creation of expanded architectures.[2]

This lecture will provide general information about zeolite structures, properties, applications and their synthesis approaches. Then, a particular focus will be centred on challenges in zeolite synthesis covering new aspects of synthesis of hierarchical materials and two-dimensional zeolites prepared by either bottom-up or top-down approaches. Finally, new synthetic protocol named ADOR mechanism (Assembly – Disassembly – Organization – Reassembly) will be presented from both experimental and theoretical perspectives.[3] ADOR has been developed for the synthesis of novel feasible and “unfeasible” zeolites and related expanded pillared materials having the same structure of the zeolitic layers but various connectivities. The principal step of the ADOR process is hydrolysis of parent germanosilicate frameworks with inherent bonding weaknesses providing layered precursors for further chemical manipulation based on intercalation and interlayer reactions. The products can be pillared materials with organic or inorganic pillars or new zeolites, some of them with unprecedented energetic features. Syntheses and structures of new materials prepared from parent UTL and UOV zeolites will be discussed.

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Dry reforming of methane over Ni-based catalysts: Advances in catalysts design

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Keywords: Ni-Al_2O_3, Ni-Au-Pt, Ni-Au-Pd, Ni-Fe, Ni-La_2O_3, Ni-perlite

Methane and CO_2 are the most abundant greenhouse gases and are the main contributors to the recent climate-change issues. The dry reforming of methane (DRM) is a chemical process that consists of converting methane and CO_2 to syngas with a H_2/CO molar ratio of 1 [1]. As a result, this process has the potentials to mitigate the environmental challenges associated with greenhouse gases emissions and to convert biogas and natural gas to syngas [2]. The syngas obtained is convenient for the production of hydrocarbons via Fischer-Tropsch reaction and for the synthesis of oxygenated chemicals [3].

Being an extremely endothermic reaction ($\Delta H_{298K} = +247$ KJ mol^{-1}), DRM requires high operating temperatures, usually in the range of 900–1273 K, to achieve the desirable conversion levels.

Despite its considerable environmental potentials, DRM is not considered an industrially mature process. The extremely high endothermic reaction, coupled with rapid carbon formation leads to the catalyst deactivation. Therefore, the design of new efficient and stable catalysts is still challenging.

Nickel is the most frequently used metal in DRM because of its good catalytic activity and its cost-effectiveness as compared with Pt, Ru or Rh-based catalysts [4]. However, the formation of significant amount of carbon coke and the particle sintering at the high temperature limit its applications. The addition of second noble metals, such as Au, Pt, Pd may reduce poisoning and deactivation [5,6]. Other solution to improve Ni catalysts lifetime is to dope with second transition metals, like Co, Fe, able to stabilize Ni as alloyed nanoparticles with enhanced resistance to coke poisoning [7]. Moreover, natural materials such as clays, phosphates and volcanic rocks are often added to Ni catalysts formulations [8].

In the present work, the performances of different catalysts used in DRM are discussed and the effect of active metals, supports and promoters are investigated for a better understanding of catalyst design.

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Benign-by-design (bio)(photo)(electro)catalysts for advanced catalytic processes

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Keywords: nanomaterials, heterogeneous catalysis, biocatalysis, electrocatalysis, photocatalysis

The design of benign and environmentally sound methodologies has been the driving force of scientists in recent years towards more sustainable methodologies. Attractive and innovative protocols that nowadays are even part of industrial ventures including biomass-derived porous carbonaceous materials, designer nanomaterials for catalytic applications and catalytic strategies for biomass/waste conversion into useful materials, chemicals and fuels have been recently developed in our group in recent years. These topics have extensively covered the preparation and design of (nano)materials, biocatalysts and photocatalysts and their utilisation in heterogeneously (bio)(photo)(electro)catalysed processes, flow chemistry as well as in biomass and waste valorisation practices [1-5].

In this lecture, we aim to provide an overview of recent efforts from the scientific community in leading the future of global scientists from chemical engineers to (bio)chemists, environmentalists and materials scientists in benign-by-design methodologies for various types of catalyst systems and key applications in bio-, photo- and electrocatalysis.

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Kinetics of reactions at solid-liquid interfaces: Solvent effects in porous catalysts

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Production of fuels and chemical feedstocks from renewable biomass requires the development of new processing strategies that differ dramatically from conventional gas phase refining. Catalytic reactions of biomass-derived molecules in porous materials take place at solid-liquid interfaces, where the local composition of the fluid phase can be very different from that of the bulk solution.[1] Many such reactions work best in semi-aqueous solvent mixtures, whose micro-heterogeneity is enhanced inside the catalyst pores. Magic-angle spinning NMR spectroscopy is a powerful emerging method for probing composition, dynamics, and reactions at solid-liquid interfaces, with high molecular specificity.[2]

The demanding reaction conditions used in hydrothermal biomass transformations are particularly challenging for NMR methods due to the presence of volatile liquids in the rapidly spinning rotor. We have developed new methods to obtain *operando* NMR spectra in chemically-resistant high pressure rotors, in order to monitor the populations of adsorbed molecules and measure the kinetics of their transformations.[3] The use of selective isotope labeling enhances sensitivity and provides mechanistic information. This system has been used to evaluate solvent effects on the kinetics and mechanism of tandem isomerization/dehydration of carbohydrates in zeolites, revealing the importance of hydrophobic partitioning. In the study of competitive hydrogenolysis/hydrogenation of lignin over supported metal catalysts, a strong solvent kinetic isotope effect revealed the role of water in catalyst activation.

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Invited Speakers

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Alternating catalytic reactions

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Keywords: oscillatory reaction, carbon monoxide oxidation, phenylacetylene carbonilation

Application of alternating current is advantageous in energy transfer over long distances. It is a well-known fact now, but subject of long conflict in the era of pioneering works in electric power production. There are also some processes in physical chemistry, organic and inorganic chemistry, in biochemistry and related sciences, which take place in opposit directions, with consecutive alternations in time. However, the very existence of alternate reactions, now known as the oscillatory reactions, has long been disputed because it was thought that it is contrary to the basic principles of thermodynamics. The first substantial applications are being explored only now, almost 100 years after the discovery of the first homogeneous oscillatory reaction. [1] This lecture will discuss the results and perspectives of such contemporary research focused on the application of alternating reactions in catalytic technologies.

Despite my long research experience I am not aware of any oscillatory reaction without catalytic loop as the essential part of a mechanism. There could be a fundamental rule that catalysis is necessary to generate oscillations in concentrations and reaction rates. Particularly, homogeneous oscillatory reactions are often subject of research as relatively simple systems with good chance to clearly define feedbacks responsible for instability phenomena. However, oscillations can at least equally often be found in heterogeneous catalytic reactions. The CO oxidation on Pt surfaces is the bright example of extensively explored heterogeneous oscillatory reaction. [2] Even direct application to sensor technology resulted from this area. [3]

More recently, interesting observation was made by Novakovic et al. [4] Product selectivity was changed during oscillatory carbonilation of phenylacetylene catalyzed by Pd(II) compounds. With this simple result, the doors are now open for wide spectrum of research projects and applications.

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Classification of reactions featuring clock behavior

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Keywords: iodine clock, autocatalysis, Landolt type reactions

When a product forms suddenly after a well-defined time lag in a chemical system, usually it is called as a clock reaction or reaction exhibiting clock behavior. The original Landolt reaction[1] (sulfite-iodine system) is autocatalytic with respect to both hydrogen and iodide ions, where the characteristics color of iodine appears suddenly only if certain stoichiometric requirements are fulfilled. Thus it seems to be straightforward that existence of stoichiometric constraints is a necessary prerequisite to categorize a reaction as a clock reaction. However, when a reaction is strongly autocatalytic with respect to a product it is also evident that formation of a product is somewhat delayed and simultaneously its formation is rapid after this well-defined time lag making it possible to characterize this reaction as a clock reaction as well.[2] The dispute over the term of clock reaction has yet not been settled[3,4] therefore a new approach to classify systems featuring clock behavior is introduced. It is proposed[5] that the well-known and recently discovered reactions featuring clock behavior can easily be categorized into three groups, substrate-driven clock behavior, autocatalysis-driven clock behavior and crazy-clock behavior. Based on real chemical systems it is shown that these groups are not distinct ones and change of the experimental conditions may easily lead to an interesting situation that classification of a chemical reaction cannot be unequivocal and may even depend on the experimental conditions as well. Consequently, we suggest that categorization based on a phenomenological approach seems to be more appropriate than the easily conceivable so called „mechanistic approach" containing the necessary requirement of a stochiometric constraint.

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Selective partial oxidation catalysts: material science at all length scales

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Keywords: catalyst development, selective partial oxidation, kinetics

Catalytic partial oxidations belong to the most challenging reactions for an industrial researcher and this not only because this class of reactions has been studied, developed, and optimized for at least 50 in some case more than 100 years. All the industrially important partial oxidation reactions have achieved a very high level of maturity, and the S-shaped learning curves have asymptotically reached their plateaus. Further improvements can only be achieved if all decisive parameters are optimized at the same time. Hence, fundamental knowledge about all details of the catalytic systems is prerequisite. Industrial partial oxidation processes especially challenge the researcher, as one has to partially beat thermodynamics kinetically stopping the reactions at the targeted value product, an intermediate on the path to CO_2. The thermodynamic equilibrium, which should be reached at the industrially often required high conversion levels, e.g. 100% in o-xylene oxidation, or >95% in case of propene oxidation, should drive oxidation reactions towards CO_2. The researcher also has to fight the high exothermicity of oxidation reactions. Insufficient heat release from the catalyst into the cooling media leads to hotspots in the reactors, often up to 100K above cooling temperature. Catalyst/reaction stability during process fluctuations is mandatory to avoid reaction run-away, the more, as these processes are nowadays often operated in the explosive regime. Optimizing heat transfer is therefore central for catalyst development. Such reactions are often affected by the pressure drop along the reactor too. The catalyst developer has to consider this during catalyst shaping, which has to be balanced with the catalyst activity demanded by the reactor productivity, and with optimum heat transport. Not only external mass and heat transport properties have to be constantly improved, this is even more important for the internal transport properties of the shaped catalysts for partial oxidation reactions. Partial oxidation reactions are often very fast and, hence, affected by internal mass transport limitations, considerably reducing catalyst activity and negatively influencing selectivity. The practitioner has to match the pore system of the catalyst body to the reaction kinetics such that maximum catalyst activity and minimum selectivity losses are achieved. Again, this optimization has to be balanced with the mechanical properties of the catalyst, which has to survive the charging procedure during change out and the mechanical stress during its service life. Every time catalyst shape or in textural properties are improved, research is started to optimize again the catalyst chemical composition and promoter levels. This next level of optimization is executed in medium to high throughput experiments in combination with μ-reactor tests to assess the intrinsic material properties. Finally, the researcher has to frequently re-align this ongoing optimization strategy as customers constantly ask for higher reactor productivities, i.e. higher space-time yields, higher feed concentrations, higher product qualities, higher tolerance for lower feedstock qualities, and of course longer service life.

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Microreactor technology as a tool for revealing kinetic and mechanistic features of catalytic reactions

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Keywords: microreactors, kinetics, oxidation, oxychlorination, hydrochlorination

A detailed knowledge of the process and reliability of the experimentally determined kinetic parameters are important for a successful design of an industrial reactor and manufacturing technology. Therefore, an accurate collection of experimental data and evaluation of kinetic parameters in laboratory scale with a reliable experimental equipment is necessary. Microreactors because of their specific properties represent suitable tools for kinetic studies. Among the most important properties for a study of heterogeneously catalyzed reactions are, for example a high internal surface to reaction volume ratio, a very precise control of operation conditions, a controlled flow the reaction mixture, low consumption of chemicals, rapid catalyst testing and a safe operation of reactions even under explosive conditions.

In the lecture several examples on application of microreactors will be considered including: oxidation and oxychlorination of ethylene, as well as hydrochlorination of methanol [1-4].

For comparison, data in conventional tubular millireactors will be also presented.

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Modified graphenes: a great challenge as support and catalysts for organic reactions

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Keywords: graphene, heteroelement doping, nano-oriented metals, selective catalytic reactions

The use of free-metal graphene in catalysis is of recent interest and represents an extension of the reported achievements in carbocatalysis. After its recent discovery, in a very short range of time, literature reported many examples demonstrating the possibility to replace noble metals (including catalysts) with graphene-based materials. These performances are also important from the perspective of the possibility to replace the fossils with renewable resources.

In this context, the lecture will report on the recent achievements of our group in the valorization of graphenes as catalysts. Graphenes, heteroelement-doped and metal deposited graphenes demonstrated an un-expected activity in a series of reactions of interest like selective hydrogenation, C-C and C-N coupling reactions [1-6]. Also, graphene oxide demonstrated a high capacity to catalyze the oxidation of amines to imines and nitriles following a modified Mars-van Krevelen mechanism [2]. In this context, orientated metal nano-platellets onto graphenes showed catalytic behavior in Ullmann, C-N and hydrosilanes coupling reactions [3] while Au in acetylation of aromatic rings [4]. The effect of these catalysts in Michael and Henry reactions will be discussed as well.

Further modification of these catalysts like treating them under cold H_2-plasma conditions provides a very efficient tool for tailoring the concentration of the defects and the strength of the active sites. This behavior will be demonstrate in a series of selective hydrogenation reactions.

Understanding the nature of the active sites and catalytic behavior of such heterogeneous catalysts requires an extensive characterization. To exemplify this, the results of characterization of fresh and tested catalysts using exhaustive ex-situ, in-situ and operando techniques like TEM, Raman spectroscopy, XPS, isotopic H_2-D_2 exchange, H_2-TPD, will be corroborated with the catalytic behavior.

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Plasma-catalytic hybrid process for CO_2 methanation: optimization of operation parameters

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Keywords: plasma, catalysis, CO_2 methanation, mechanism, operating conditions

The future regulations in greenhouse gases emissions (mainly CO_2) lead the society to find efficient processes for the stabilization of atmospheric CO_2. Among the different processes, such as reutilization as an alternative to its geological storage, the catalytic valorization of CO_2 methanation, i.e. CO_2 hydrogenation, stands as a promising and industrial-scale applicable technology. $CO_2 + 4H_2 = CH_4 + 2H_2O$ (ΔH = - 165 KJ/mol)[1,2]. Although CO_2 conversion into methane is exothermic and thermodynamically favorable at ambient temperature, a catalyst and high temperatures (> 350°C) are needed in order to achieve acceptable methane yield. Though many different metals have been used to catalyze the methanation process, the catalysts mostly based on Group VIII metals, such as Ni and Ru mainly supported on porous supports, are the most developed catalytic systems [3-7]. Ni-based catalysts have been widely investigated, because of their good compromise between activity and economics [7]. In order to decrease the operating temperature, the association of a catalyst with a non-thermal plasma have been recently proposed, using a dielectric-barrier discharge plasma (DBD) [8] as a tool for improving the CO/CO_2 methanation reaction. Non-thermal plasma, producing a wide variety of active species such as electrons, ions and radicals, has been applied to the methanation of CO_2. Optical emission spectroscopy (OES) is a powerful diagnostic tool widely used for the characterization of different types of plasmas. It allows the partial determination of the plasma composition without exerting any intrusion or influence over it. Moreover, OES provides crucial information about the excitation state (vibrational and rotational), the electronic temperatures and the energy distribution and thus can be used in order to know the contribution of plasma to the overall reaction mechanism such as CO_2 methanation. Moreover, among the different coupled DBD plasma catalytic systems, Ni-containing zeolite, ceria-zirconia supported Ni or hydrotalcite-based Ni catalysts [8] led to the better performances. However, the plasma parameters were never optimized in order to find the best compromise between energy efficiency and performance. In the present work a hybrid plasma-catalytic process at atmospheric pressure was tested for low temperature CO_2 hydrogenation with two catalysts (ceria-zirconia supported nickel and hydrotalcite-supported nickel). Thus, the power was measured vs. the voltage. The power was also measured as function of temperature. Optical Emission Spectroscopy was used to determine the excited species present in the plasma during plasma-catalyst interaction. The coupled plasma DBD – Ni/$CeZrO_2$ system leads to high CO_2 conversions into methane without any external heating source. However, the influence of plasma parameters is similar for both catalysts with an optimal performance for 15kW. The low temperature activity is linked with the formation of highly reactive species from CO_2 and H_2 in the presence of the plasma, able to react easily on the surface of the Ni/$CeZrO_2$ catalyst

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Strong metal-support interactions in supported gold catalysts and their application in catalysis

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Keywords: strong metal-support interaction, gold nanoparticle, hydroxyapatite, titanium oxide

The strong metal-support interaction (SMSI) between Au nanoparticles (NPs) and hydroxyapatite (HAP) was discovered for the first time by our group [1]. The characteristics of this SMSI are identical to the classic SMSI between TiO_2 and platinum group metals (PGMs), except that it occurred under oxidative atmosphere. The SMSI in Au/HAP not only enhanced the sintering resistance of Au NPs but also improved the selectivity and reusability in liquid-phase reaction.

Through the SMSI between Au and HAP, the encapsulation of Au NPs by HAP like thin layer improves their sintering resistance significantly. However, the encapsulation of the Au NPs reduces their activity due to the coverage of the active sites. In order to minimize this disadvantage, we tuned the encapsulation degree of Au NPs by preparing TiO_2-HAP composited support and successfully developed an ultrastable and highly active gold catalyst, Au/TiO_2-HAP [2]. It is interesting that in this catalyst the Au NPs were located at the interfacial regions between TiO_2 and HAP. Due to this unique nanostructure, the surface of Au NPs was partially encapsulated and partially exposed and accessible to the reaction molecules. The SMSI between Au and HAP helped to stabilize the Au NPs while the partially exposed surface of Au NPs provided the active sites for reactions. Such a catalyst not only demonstrated high activity even after calcination at 800 °C but also showed excellent durability for a series of high-temperature reactions.

Conventional wisdom holds that supported Au catalysts are difficult to manifest classical SMSI. Very recently, the discovery and systematic identification of classical SMSI between Au NPs and TiO_2 has been reported for the first time by our group [3]. The results of multiple characterizations showed that the characteristics of this SMSI between Au NPs and TiO_2 are identical to the classical SMSI which occurred on the TiO_2 supported PGMs. It was further identified that the same SMSI can be existed in other reducible oxides (such as Fe_3O_4 and CeO_2) supported Au catalysts and TiO_2 supported other IB metal such as Ag and Cu.

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T1: Catalysts in sustainable and green chemistry

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Catalytic processing of plant waste resulting in formation of useful products

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Keywords: oxidative catalysis, kinetics, hydrogen peroxide, biomass, lignobiomass, iron(III) oxides, plant growth stimulation

For some years, new flexible, environmentally benign, catalytic process for the waste-free recycling of plant residues into useful products was developed. Colloidal catalytic system based on iron (III) oxides combined with environmentally friendly oxidants - hydrogen peroxide and/or atmospheric oxygen was successfully used for processing of lignocellulosic biomass under atmospheric pressure at mild temperature 60-70°C [1-3].

The catalyst is based on iron (III) oxides, obtained by hydrolysis of Fe (III) salts in water in the presence of a surfactant. It decomposes H_2O_2 actively and catalyzes the oxidative destruction of lignobiomass under atmospheric pressure in water media. The oxidative destruction of biomass results in formation of light organic acids, esters and other low molecular oxidation products derived from lignin, hemicelluloses, cellulose, lipoproteins and sugars. The solid product, which constitutes mainly of pure cellulose and its derivatives, can be used as a filler and carrier in the cosmetic, food and pharmaceutical products. Water-soluble oxidation products are found to regulate the growth of agricultural plants [4,5]. The comparison of catalytic H_2O_2 decomposition during oxidative treatment of various biomass (conifers saw dust, peat, oat straw, olive marc, flax fire and technical lignin) taken at equal percentage conditions, shows that biomass retards the rate of H_2O_2 consumption, however, in different extent. The study of catalytic mechanism has shown that the initial nanosized catalyst, completely adsorbed on the biomass surface, is transformed depending from biomass nature and reaction conditions. The degree of oxidative cracking and depth of organic material conversion can be regulated by the reagent concentration ratio and the processing time

The same slightly modified technology has been tested for processing of dry oak and maple leaves. We hope that a great number of dry leaves can be converted into decontaminated useful for soil products instead of burning leaves in spring and autumn. Because leaves contain a considerable amount of hydrophobic Thus, the application of catalytic oxidative treatment of waste biomass facilitates the solution of two problems: the utilization of agricultural wastes and the improvement of the agricultural, and greenhouse soils by returning to the soil the chemicals needed by the plants. Surface substances, the solid residue of catalytic processing of leaves differs from the cellulose-like solids resulted from wood biomass treatment. Its structure reminds the plant polymers cutin and suberin; it may be used as light filler for polymer composites. However, liquid water-soluble oxidation products were found to affect the growth of plants.

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Highly active and stable zirconium phosphate grafted on KIT-6 for renewable *p*-xylene production via cycloaddition of biomass-derived intermediates

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Keywords: zirconium phosphate on KIT-6, *p*-xylene, cycloaddition reaction, sustainable chemistry

A biorefinery technology is an important approach for current production needs of renewable energy and chemical building blocks, and *p*-xylene (PX) is considered as an important building block for terephthalic acid that can be used as monomer for polyester and polyethylene terephthalate plastics.[1] The Diels–Alder cycloaddition of 2,5-dimethylfuran (DMF) with ethylene, and a subsequent dehydration of the cycloadduct intermediate is an attractive reaction, since this route is considered as a fully sustainable process for the production of PX. The reported H-Y and Zr-BEA zeolite, although displayed a good DMF conversion with 75-80% PX selectivity, can catalyze an unwanted alkylation and isomerization reaction in the presence of higher DMF concentrations (>1.0 M), which not only reduce the PX selectivity but also lead to fast catalyst deactivation.[2] In view of the overall reaction rate and stability, the catalysts having Lewis (L) and Brønsted (B) acid sites with high specific surafce area are highly needed for this tandem reaction.

In the present study, one-pot grafting of zirconium phosphates on KIT-6 (Zr_xP_y-KIT-6, where x and y are theoretical molar ratio of Zr and P) were studied for PX production from DMF with ethylene throguh cycloaddition reaction. A low angle XRD of Zr_xP_y-KIT-6 showed the characteristic 3D cubic (KIT-6) structures having d_{112} plane, which shifted to a lower angle with increaing Zr to P ratio (Fig. 1(a)). The representative HRTEM image (Fig. 1(b)) confirmed that the cubic architectures of KIT-6 were retained even after grafting of ZrP. The ZrP-KIT-6 displayed a maximum DMF conversion of 85% with 95% selectivity of PX, which was significantly higher than microporous H-Y and HZSM-5 catalysts (Fig. 1(c)). The high and stable catalytic performance for PX production on the ZrP-KIT-6 may be attributed to the higher surface area, pore diameter and ordered mesoporous structure with complete absence of micropores along with more number of the accessible B and L acid sites.

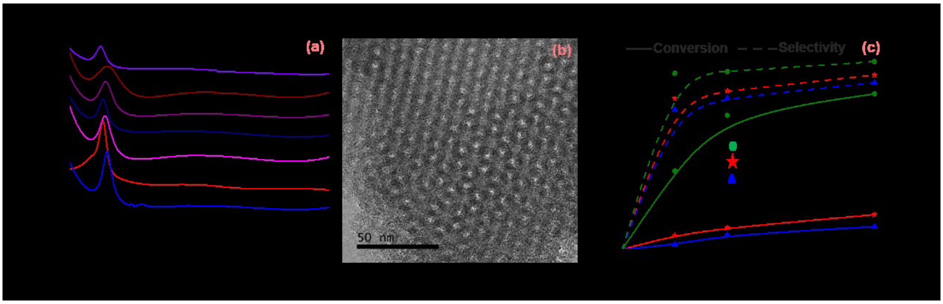

Fig. 1 (a) Low angle XRD patterns of Zr$_x$P$_y$-KIT-6, (b) representative HRTEM image of the ZrP-KIT-6, and (c) catalytic activity of the ZrP-KIT-6 and H-Y and HZSM-5 [*Reaction conditions*: DMF = 2.35 M; catalyst = 0.14 g; temp. = 250 °C; ethylene = 20 bar]

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Catalytic peroxide fractionation processes for the green biorefinery of wood

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Keywords: catalysts, peroxide fractionation, hardwood, softwood, cellulose, soluble products

Significant resources of lignocellulosic biomass are presented by wood which can be used as an important renewable feedstock for production of valuable chemicals and biofuels. The promising approaches in the development of green biorefinery of wood into valuable chemicals and biofuels are based on the fractionation of main components of lignocellulosic biomass – polysaccharides and lignin.

This presentation described the optimized green processes of catalytic peroxide fractionation of hardwood and softwood on cellulose and soluble products from lignin and hemicelluloses.

Air dry sawdust of aspen, birch, abies, larch and pine wood were used. Catalytic processes of wood peroxide oxidation were studied with the use of stirring fixed-bed reactor. FTIR, XRD, SEM, NMR and chemical methods were used for study the solid products. Soluble products were identified by GC, HPLC, and GC-MC methods.

Among the tested catalysts (H_2SO_4, H_2MoO_4, Na_2MoO_4, TiO_2) the suspended catalyst 1% TiO_2 was selected for detail study in the processes of peroxide fractionation of hardwood and softwood in the acetic acid – water medium at the temperature range 70-100 °C.

The catalyst TiO_2 in rutile modification has the higher activity in wood peroxide delignification at 100 °C as compared to TiO_2 in anatase modification. The results of kinetic studies and optimization of the processes of peroxide depolymerization of hardwood (aspen, birch) and softwood (abies, larch, pine) lignins in the medium of acetic acid – water over catalyst TiO_2 (rutile) are compared. The catalyst TiO_2 initiates the formation of $OH^{\bullet}$ and $OOH^{\bullet}$ radicals from H_2O_2 which promote the oxidative fragmentation of wood lignin. In this case, the peroxide depolymerization of softwood lignin, constructed from phenylpropane units of guaiacyl-type proceeds more difficult than the hardwood lignins, also containing syringyl-type units.

For all type of wood the processes of peroxide fractionation are described by the first order equations and have the activation energies 76-86 kJ/mol. The optimized conditions of wood fractionation processes were established by experimental and mathematical methods.

Regardless of the nature of wood the cellulosic products of peroxide delignification have a structure similar to microcrystalline cellulose. The soluble products mainly consist of monosaccharides and organic acids. Aromatic compounds are present only in a low amount which indicates the oxidative degradation of aromatic rings of lignin phenylpropane units under the used process conditions.

The scheme of green biorefinery of wood was suggested which based on wood peroxide catalytic fractionation on cellulose and soluble products from lignin and hemicelluloses. The catalytic biorefinery of wood makes it possible to achieve the utilization of all main components of woody biomass by environmentally friendly way.

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Use of isotopic tracers to obtain mechanistic understanding in the conversion of lignin to alkylphenol monomers

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Introduction

Lignin is the most recalcitrant part of woody biomass yet is one of the few natural aromatic resources available in abundance. There is huge potential for this material to be used as a key feedstock in future applications however a conversion route to fine chemicals must be first be established. In previous papers [1, 2] we reported on how four lignin preparations from poplar and wheat straw were found to have different S:G:H ratios and contents of alkyl–aryl ether bonds and how this feedstream history affected depolymerisation using a Pt/alumina catalyst. In this paper we continue our investigation of lignin depolymerisation using deuterium and deuterated solvents to probe the mechanism of the process.

Experimental

Lignin samples were prepared by ammonia pretreatment [1]. The Pt/Al_2O_3 catalyst was supplied by Johnson Matthey. The catalyst was reduced *ex situ* at 523K. Reactions were carried out in a 300 ml Parr autoclave. Typical reaction conditions were 0.5 g lignin, 0.1 g catalyst, 100 ml H_2O/MeOH (50:50) solution, 20 barg hydrogen and 300C. Reactions were also carried out using D_2, D_2O and CD_3OD and mixtures thereof. The autoclave was sealed, purged and charged with 20 barg H_2 and heated to the desired temperature for 2h (with an additional 30min ramp time). After cooling the mix was filtered and any remaining material solubilised in acetone. The H_2O/methanol soluble fraction was centrifuged and acidified to pH3 and products removed using a solvent-solvent extraction method. Soluble products were analysed using a Shimadzu GC-MS-QP2010S coupled to a Shimadzu GC-2010 equipped with a ZB-5MS capillary column (30m x 0.25mm x 0.25 μm) and FID detector. C-16 was used as an internal standard.

Results and Discussion

The mechanism of the reaction was probed using deuterium, deuterated water and d_4-methanol. Analysis focused on alkylphenol products. Interestingly when a completely deuterated reaction was performed instead of a protiated reaction an inverse kinetic isotope effect (KIE) was observed (Fig.1) with a higher yield being obtained from the deuterium system (22 %) compared to the protiated system (16 %). There was a general increase observed for each of the products with no dramatic change in selectivity for most products, although there was an increase in selectivity towards the unsaturated 2-methoxy-4-propenylphenol and 2,6-dimethoxy-4-propenylphenol products and a subsequent decrease in the saturated 2-methoxy-4-propylphenol and 2,6-dimethoxy-4-propylphenol products due to the monomers being able to retain the C=C bond when deuterium was used to the reaction. If deuterium gas is used to replace hydrogen gas and the solvents remain protiated there is no change in the yield indicating that the gas phase hydrogen is not involved in the rate determining step. On the contrary when methanol is replaced by d_4-methanol, an inverse KIE is observed similar to that seen when all the components are deuterated. The extent of deuterium incorporation in the products is also dependent upon the deuteration of the solvent. For example with 2,6-dimethoxy-4-propylphenol when D_2O is present six D atoms are incorporated into the molecule, whereas when D_2O is absent, even if D_2 and CD_3OD are present, there is no deuterium incorporation. Detailed analysis of the fragmentation patterns has allowed determination of which positions in the molecules have deuterium rather than protium.

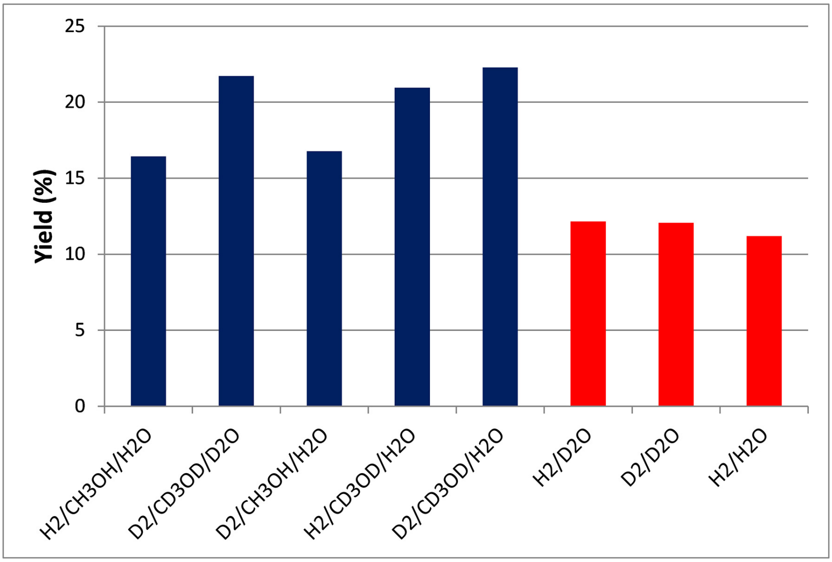

Figure 1. Alkylphenol yield observed with different isotopic solvents.

Conclusions

The work has allowed us to delineate the roles of solvent and gas in the hydrogenolytic depolymerisation of lignin. It has also given useful mechanistic information that can be used to understand the processes occurring under reaction conditions.

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Effect of the support nature on the activity and selectivity of palladium catalysts in the aqueous-phase hydrogenation of furfural

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Keywords: furfural, catalytic hydrogenation, palladium catalysts

The effect of the support nature (carbon nanotubes, carbon nanoglobules, alumina, mixed MgAl oxide) and Pd loading (0.5, 1, 2 wt. %) on the activity of palladium catalysts and the reaction routes of aqueous-phase hydrogenation of furfural (423 K, 3 MPa, 1 h) was investigated. It was found that the carbon-supported catalysts containing 1 and 2 wt. % Pd are the most active in the reactions under study. In the presence of these catalysts, almost complete conversion of furfural is achieved and water facilitates the opening of the furan ring. As a result, the selectivity for products of acid-base reactions involving water is increased. Among these products, the main are 4-oxopentanal (selectivity up to 63 %) and cyclopentanone (selectivity up to 57 %).

Catalysts based on the oxide supports (γ-Al_2O_3, $MgAlO_x$) are much less active in hydrogenation and complete conversion of furfural does not occur (up to 55 % in the presence of the most active 2 % Pd/γ-Al_2O_3 catalyst). In the presence of catalysts prepared using basic support (MgAl oxide), there are no reactions involving water and the main products are furfuryl alcohol (selectivity up to 78 %) and tetrahydrofurfuryl alcohol (selectivity up to 26 %). Based on NMR analysis of the reaction mixtures, a scheme of transformations during the catalytic hydrogenation of furfural in an aqueous solution is proposed (Fig. 1).

The results can be useful for the development of efficient palladium catalysts for hydrogenation of biomass-derived furfural to valuable chemicals.

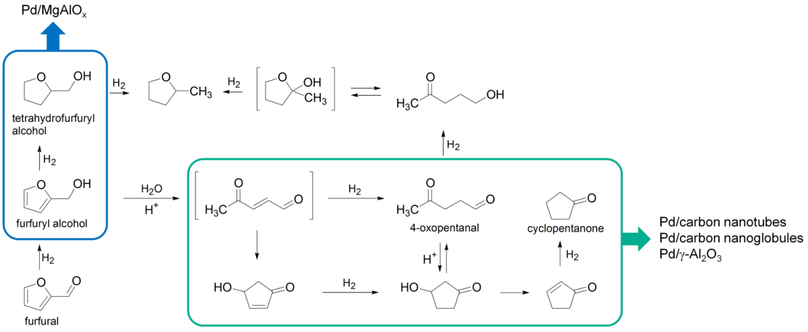

Fig. 1. Reaction pathways of aqueous-phase hydrogenation of furfural over supported palladium catalysts

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Levulinic acid hydrodeoxygenation over silica-supported Co catalysts

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Keywords: levulinic acid, hydrodeoxygenation, bifunctional catalysts

Lignocellulosic biomass is continuously renewed having the potential to become the carbon source of sustainable production of fuels and chemicals. It is relatively easy to obtain levulinic acid (LA) from lignocellulose with a yield, high enough to be platform material of the chemical industry. LA can be converted to γ-valerolactone (GVL) in consecutive hydrogenation and dehydration reactions. Controlling catalytic selectivity GVL hydrogenolysis can be directed to give either 1,4-pentanediol (1,4-PD) or pentanoic acid (PA). Cyclodehydration of 1,4-PD leads to 2-methyltetrahydrofuran (2-MTHF). GVL and 2-MTHF are potential fuel additives and green solvents. The conversion of LA to GVL is widely studied and reported to occur rapidly with good yields over heterogeneous noble and transition metal catalysts [1]. However, only few publication reports direct conversion of LA to 2-MTHF [2]. The present study concerns solvent-free LA hydrodeoxygenation (HDO) reaction, over silica-supported Co catalyst.

Catalysts Co/SiO_2 was prepared by the wet impregnation of silica CAB-O-SIL M5. Preparations were characterized by *ex situ* and *in situ* XRD. Chemisorption of CO was studied by transmission FT-IR spectroscopy to learn about the electronic state of the active species. The cobalt dispersion was determined by the H_2-chemisorption method. Temperature-programmed reduction by hydrogen (H_2-TPR) was used to examine the redox properties of the catalysts. Acidity was characterized by the FT-IR spectra of adsorbed pyridine. A continuous flow-through fixed-bed microreactor was used at 30 bar total pressure in the 200-300 ^{o}C temperature range to study the LA HDO reaction. Molecular hydrogen was applied as reducing agent.

Results show that silica-supported Co catalysts catalyze the LA to GVL reaction through angelica lactone (AL) intermediate. The enol or cyclized form of LA is first dehydrated to α-angelica lactone and then the hydrogenation of the C=C double bond of AL leads to GVL. At the early stage of time-on-stream (TOS) large amount of 2-MTHF were also found in the product, suggesting the product GVL was further converted to 2-MTHF *via* 1,4-PD. The activity of the catalyst decreased in the hydrogenolysis of GVL and even stopped after 12 hours TOS at 200 ^{o}C. As a result only GVL was formed with a selectivity of virtually at 100 % at full LA conversion. At reaction temperature 225°C the LA conversion remained full but the GVL selectivity dropped. Mainly 2-MTHF (with 65 % yield) and small amount of alcohols were found in the product mixture.

By tuning the reaction conditions it can be attained that either γ-valerolactone or 2methyltetrahydrofuran product should be obtained from levulinic acid over the studied non-noble-metal catalyst with high yield.

Acknowledgments

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Hydrogenation of hydroxy-substituted naphthalenes using Ru catalysts

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Keywords: Ru catalyst, hydrogenation, 1,5-dihydroxynaphthalene, 1,8-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, 2,7-dihydroxynaphthalene

The desired product of 1,5-dihydroxynaphtalene total hydrogenation is decalin-1,5-diol, compound used for different polymers and fine chemicals preparation [1,2]. Under conditions conventionally used for hydrogenation of napht-1-ol or napht-2-ol (5% Ru/C, temperature 170 °C, pressure 15 MPa) hydrogenolysis of CO bond takes place only to a small extent. On the other hand, under the same conditions one of CO bonds has been found to be hydrogenolyzed during 1,5-dihydroxynaphtalene hydrogenation and the main detected product was 1-decalol instead of the desired decalin-1,5-diol. The influence of reaction conditions on hydrogenation of various dihydroxy-substituted naphthalenes (1,5-dihydroxynaphthalene, 1,8-dihydroxynaphthalene, 2,6-dihydroxynaphthalene and 2,7-dihydroxynaphthalene) has been studied. The influence of the position of hydroxyl groups on CO bond hydrogenolysis has been evaluated. Suitable reaction conditions have been sought to obtain decalindioles with the highest selectivity. The presence of the alkaline diluent together with Ru catalysts positively influenced hydroxy-substituted and polyhydroxy-substituted aromatic hydrocarbons hydrogenation without detectable hydrogenolysis occuring [3]. The highest selectivity to desired dihydroxy-substituted decalins was obtained in case of 2,6-dihydroxynaphtalene and also the highest reaction rate was achieved in this case.

Acknowledgments

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Syngas production over Ni/yttria-doped layered double hydroxides catalysts

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Keywords: dry reforming of methane, nickel, yttrium, layered double hydroxides

Dry reforming of methane (DRM) is considered one of the promising CO_2 utilization methods, yielding to syngas, which is currently used as feedstock in liquid fuel production processes, such as Fischer-Tropsch or methanol synthesis. However, the DRM has not yet been launched on industrial scale mainly due to the lack of a stability and selectivity of proposed catalysts [1]. Among the most widely studied materials, the Ni catalysts on different supports have been considered suitable candidates for DRM due to high availability, low cost, and promising catalytic performance. The main drawback of the possible application of such materials is the predisposition to fast deactivation mainly due to carbon formation and the sintering of active phase [2]. Many supports have been studied in literature, among them, layered double hydroxides (LDHs), which showed promising performance in DRM because they may form mixed nanooxides, and they have basic properties and the ability to exchange anions of the layers [3]. In the literature, different metals (Ce, La, Y) deposited on oxides supports have shown to be active and stable in DRM. It was also shown that the substitution of Ni^{2+} ions by Y^{3+} leads to higher catalytic stability, because of the formation of oxygen vacancies, the latter resulting in the elimination of carbon deposits [4].

In this study, Ni/Mg/Al-LDHs were doped with yttrium (0.2 and 0.4 wt.%) and tested in DRM. Physicochemical characterization, such as: XRF, BET analysis, XRD, TPR-H_2 and TPD-CO_2 showed that the introduction of yttrium led to: (i) a stabilization of specific surface area, (ii) smaller Ni^o crystallite size, (iii) a decrease in reducibility of the nickel, and (iv) a higher distribution of weak and medium basic sites compared to the strong ones in the modified LDHs. The methane reforming tests were carried out in a fixed-bed quartz reactor at atmospheric pressure from 600 to 850ºC, under following conditions: 100 ml/min total flow rate with $CH_4/CO_2/Ar=1/1/8$ and a GHSV=20,000h^{-1}.

An enhancement in catalytic activity was observed for Y-modified catalysts.

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Heterogeneous acid catalysts for preparation of substituted tetrahydropyranols

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Keywords: tertrahydropyranol, acid catalyst, heteropolyacids, montmorillonite K10

Tetrahydropyranic structure may be found in many biologicaly active compounds including compounds with antiinflamatory or analgetic activity or important fragrant compounds. The simplest way for the preparation of this structure is Prins cyclization, acid catalyzed reaction of aldehyde and homoallylic alcohol. As acidic catalyst of this reaction many Lewis and Brønsted acids were applied, including only few heterogeneous or heterogenized ones [1-4]. The comparison of different heterogeneous catalysts in Prins cyclization of isoprenol and isovaleraldehyde as a model reaction was offered in this work. The chosen catalysts were montmorillonite K10, iron modified silica and aluminosilicates, molybdenum modified silica and aluminosilicates and heteropolyacids heterogenized on mesoporous silica. All catalysts except montmorillonite K10 were prepared and characterized by available methods. Under comparable reaction conditions (70 °C, molar ratio of reactants 1:1, 10 wt.% of catalyst) the highest selectivity to substituted tetrahydropyranol was obtained using heterogenized phosphomolybdic acid (up to 96 %). Using other mentioned catalysts the selectivity to desired compound was comparable and ranged in region 60 - 70 % dependently on acidity of used catalyst. All catalyst were reused in the mentioned model reaction with no loss of selectivity. These catalysts may serve as successful catalysts for Prins cyclization in fragrant industry. Especially heterogenized heteropolyacids offered high selectivity to desired compound and montmorillonite K10 represented simple and available catalyst for this reaction.

Acknowledgments

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Poster

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CO hydrogenation to hydrocarbons on zirconium phosphate (ZrP)-modified Co/KIT-6

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Keywords: Fischer-Tropsch Synthesis, cobalt, mesoporous KIT-6, zirconium-phosphate modification, stability

Fischer-Tropsch Synthesis (FTS) reaction is a kind of chemical conversion process to convert syngas to a wide range of value-added hydrocarbons. The ordered mesoporous Co/KIT-6 catalysts were modified with zirconium phosphate (ZrP) to improve the catalytic activity and structural stability. At an optimum molar ratio of P/Zr of 0.2, the CoZrP/KIT-6 showed the highest catalytic stability and CO conversion through a spatial confinement effect of cobalt nanoparticles in the matrices of the well-dispersed ZrP nanoparticles as shown in Figure 1 and Table 1. These ZrP nanoparticles suppressed the aggregations of cobalt nanoparticles and the formation of inactive heavy coke precursors, which were the main reasons for catalyst deactivation during FTS reaction.

Table 1. CO conversion and product distribution on the CoZrP/KIT-6 catalysts[a]

`	CO conv. (C-mol%)	Product distribution (C-mol%)					Ole sel.[b] (C-mol%)	Chain growth probability (α)[c]	
		CH_4	C_2-C_4	C_5-C_{10}	C_{11}-C_{19}	C_{20+}		C_{11}-C_{19}	C_{20+}
CoSi	30.0	25.5	17.3	26.5	23.4	7.3	29.7	0.95	0.83
CoZrP(0)/KIT-6	6.8	42.8	44.8	12.4			40.5	N.A.	
CoZrP(0.1)/KIT-6	21.9	42.7	36.8	20.5			50.1	N.A.	
CoZrP(0.2)/KIT-6	43.8	19.4	16.4	24.3	30.1	9.8	40.0	0.94	0.84
CoZrP(0.6)/KIT-6	35.4	16.9	13.6	22.7	35.4	11.4	40.0	0.95	0.85
CoZrP(2)/KIT-6	24.5	19.7	14.9	25.4	28.3	11.7	43.1	0.95	0.90

[a] Catalytic performances were evaluated using the averaged values at a steady-state under the reaction conditions of T = 230°C, P = 2.0 MPa, WHSV = 8000 $L/(kg_{cat}\cdot h)$, and $H_2/CO = 2$.

[b] The olefin selectivity was obtained in the C_2-C_4 light hydrocarbons.

[c] The chain growth probability (α) was calculated using the Anderson-Schultz-Flory (ASF) distribution.

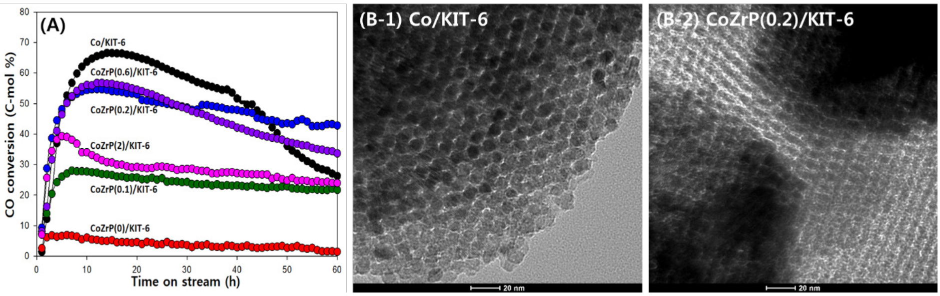

Figure 1. (A) CO conversion with time on stream (h), (B) TEM images of the (1) Co/KIT-6 and (2) CoZrP(0.2)/KIT-6

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Photocatalysis on sodium dodecylbenzenesulfonate model wastewater over dye sensitized TiO_2–chitosan layer

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Keywords: dye-sensitized photocatalysis, photocatalytic films, Sodium dodecylbenzenesulfonate TiO_2, water purification

The main goal of this research was to explore the possibility of the photocatalytic activity enhancement by introducing the different types of dyes and pigment and their mixture in the photocatalytic films.

Selected dye (Basic blue 1), pigment (Imperon Orange K-RC) and commercial TiO_2 powder (AEROXIDE® P25) were integrated within the matrix of chitosan molecules as a thin layer films and immobilized on different type of support. Efficiency of the photocatalytic oxidation of the surfactant natrium dodecylbenzene sulfonate (SDBS) has been evaluated for each applied film, based on the colorimetrically determined SDBS concentration. The development and a partial characterization of the supported catalyst were described within this study.

Experiments were performed in a batch laboratory reactor and the effect of pH, different light sources (low-pressure mercury lamps, Xenon lamp) and type of support were investigated and the optimized conditions for maximum amount of degradation were determined. In order to evaluate the possibility of using the natural light source, the additional set of experiments at optimal conditions has been performed in the boat flow reactor under direct sunlight.

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Experimental study and kinetic modeling of the transformation of ethanol and acetaldehyde mixture into butadiene

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Butadiene is a chemical molecule of interest for the production of synthetic rubbers such as styrene-butadiene or polybutadiene. Due to a growing demand and a reduction in its production capacity from fossil fuels, alternative routes to synthesize this compound have recently recorded a growing interest.
One of them uses bio-based ethanol as raw material. Historically, two versions of this transformation have existed: the one-step and the two-step processes, also called the Lebedev and the Ostromislensky process respectively. The latter consists of partial conversion of ethanol into acetaldehyde in a first reactor before converting an ethanol / acetaldehyde mixture into butadiene in the second stage (see Figure 1).

Regarding this reaction, different schemes have already been proposed in the literature. The most accepted was described by Jones [1]. It involves an aldol condensation of two acetaldehyde molecules followed by crotonization, Meerwein-Ponndorf-Verley type reduction reaction and then dehydration (see Figure 2).

While this mechanism is commonly accepted, it is not fully demonstrated. Other pathways have been proposed through reactions such as the Prins reaction [2] or intra-molecular hydrogen transfer [3]. The objective of the study is to identify the chemical pathway(s) and to develop a kinetic model for the production of butadiene from an ethanol / acetaldehyde mixture.

In order to develop the kinetic model, the reaction scheme is studied by means of fixed bed type catalytic tests involving various reagents and reaction intermediates assumed to exist, including those proposed in the reactions mentioned above. The reactor (gas / solid, isothermal and isobaric) is modeled in steady state by taking into account gaseous diffusion and axial dispersion. If needed, external and internal diffusional limitations as well as thermal effects can also be modeled. An optimizer is developed to determine the kinetic parameters by fitting the model on the experimental results.

Figures

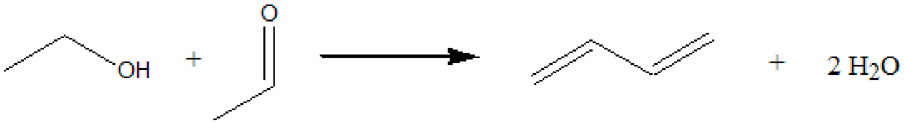

Figure 1. Overall reaction of transformation of ethanol / acetaldehyde mixture to butadiene

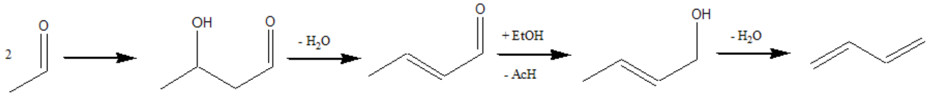

Figure 2. Jones reaction pathway [1]

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Copper-catalyzed Ullmann and Chan-Evans-Lam reactions of the C-S bond formation in the derivatives of 5-arylidene-2-thioxoimidazolin-4-one

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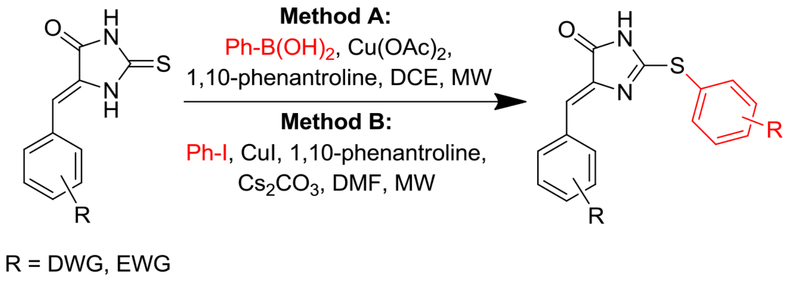
Keywords: copper-catalyzed reactions, Ullmann reactions, Chan-Evans-Lam reactions, C-S coupling, thio-amides, arylboronic acids, aryl halides

Derivatives of hidantoin and 2-thiohidantoin have found wide application in the design of non-steroidal antiandrogen drugs. In the treatment of prostate cancer nilutamide, proxalutamide, enzalutamide and apalutamide are widely used. In all these preparations, the active substance contains a hydantoin and 2-thiogidantoin fragment in its structure. Unlike antiandrogens of the previous generation, enzalutamide inhibits the translocation of the androgen receptor into the nucleus of the cell and prevents the binding of the receptor to DNA and co-activating proteins [1].

In this study two methods were applied for the S-arylation of 2-thiohidantoin derivatives. At first, we decided to apply a method, developed in the previous study for modification of (Z)-5-arylidene-3-aryl-2-thioxoimidazolin-4-ones [2]. Now (Z)-5-arylidene-2-thioxoimidazolin-4-ones (with non-substituted nitrogen atom) were taken as the starting material.

For the synthesis of (Z)-4-arylidene-2-(arylthio)-1H-imidazole-5(4H)-one derivatives, we used two nominal reactions – Chan-Evans-Lam (Method A) and Ullmann reactions (Method B).

In this study, we have developed a novel simple and inexpensive method for the copper-catalyzed S-arylation. We synthesized a library of 2-thiogidantoin derivatives, based on the results of molecular docking. This new approach leads to compounds in which the nitrogen atom does not contain aromatic substituents so that can improve anti-cancer activity and solubility in a physiological environment, in contrast to the known hydantoin antiandrogens.



Synthesis of (Z)-4-arylidene-2-(arylthio)-1H-imidazol-5(4H)-ones

Acknowledgments

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Novel waste polymer based activated carbons as catalyst support

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Keywords: activated carbon, catalysts, methanol decomposition

Activated carbons have been considered during the last decades for utilization in several processes involving heterogeneous catalysis, due to their suitable surface properties, thermal stability, adequate mechanical properties, tunable specific surface area and porosity [1, 2]. In our previous study we demonstrated possibilities for using activated carbon based on biomass residues as a host matrix for nanodispersed transition metal species [3]. This study is focused at the preparation of novel activated carbons from waste polymers mixtures (polymers and used motor oil or by-products from coal tar pitch treatment) investigation of their potential as catalyst support.

For the purpose, zinc ferrite are used as catalytic active phase and the catalytic behaviour of the obtained composites is tested in methanol decomposition. For more precise discussion, similar reference samples based on activated carbon from peach stones and polyolefin wax and mesoporous silica type KIT-6 are used. Nitrogen physisorption, Boehm method, XRD, TPR with hydrogen, FTIR, UV eVis and Moessbauer spectroscopy were applied to investigate the activated carbon characteristics and the state of loaded metal oxide particles. The catalytic behaviour of the samples was tested in methanol decomposition to syngas. The interest to methanol decomposition is strongly related to the perspective methanol (including biomethanol) to be used as easily transportable and safety storage reservoir of hydrogen or synthesis gas. However the main challenge in this aspect is the preparation of low cost, but highly active and selective catalysts which can release hydrogen from methanol in case of need even at relatively low temperatures.

The obtained novel activated carbons, could be used as a host matrix for the stabilization of nanosized zinc ferrite nanoparticles. The preparation procedure and the precursor used results in fine tuning of surface and textural characteristics of the obtained activated carbons, which reflects on the state of loaded metal oxide species. Zinc ferrite modifications of both novel activated carbons exhibited high catalytic activity, stability and good selectivity to syngas in comparison with the individual metal oxide ones.

Acknowledgments

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Copper-zinc ferrite nanoparticles hosted in mesoporous titania doped with zirconia, ceria and tin binary oxides as catalysts for sustainable environmental protection

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Keywords: binary oxides, catalysts, copper-zinc ferrite, environmental protection

Recently, the energy crisis and the increased environmental problems have gained a considerable interest towards the development of integrated fuel cell processors, supplied by liquid fuel, which can release hydrogen in case of need [1]. Safe and efficient in situ hydrogen generation from methanol can promote the use of fuel cells and other technologies as a source of clean energy for many applications. Since methanol can be produced easily from biomass by well-developed technologies [2], it is a potential renewable fuel that can be reformed onboard to generate hydrogen. Among the various reforming processes, methanol decomposition is the simplest one producing syngas. The development of active and low-cost catalysts for methanol decomposition forced their usage in nanoscale by deposition on suitable, generally porous supports. Transition metal oxides could be a promising alternative of the more expensive noble metals and among them titanium oxide has received much attention in various technological areas, due to its superior electrical, optical, and photocatalytic properties. The preparation of nanodispersed mesoporous TiO_2 as well as its doping with different metal oxides provides much opportunities not only to improve the catalytic behavior, but also to form new stable compounds, which could lead to completely different physicochemical and catalytic properties.

The aim of current investigation is to develop a series of nanosized mesoporous binary materials on the base of the promoted with Ce, Zr and Sn titania as host matrix for copper-zinc ferrite nanoparticles and to test them as catalysts in various processes, which are important both from the energy and environmental point of view, such as methanol decomposition to hydrogen and total oxidation of ethyl acetate. The obtained materials were characterized by low temperature nitrogen physisorption, XRD, SEM, TEM, Raman, UV-Vis, FTIR and thermo-programmed reduction with hydrogen.

Mesoporous nanostructured binary materials are successfully synthesized using template assisted hydrothermal technique. Binary oxides supports exhibit improved dispersion, high surface area and pore volume. The additives of copper-zinc ferrite to binary oxides promotes their catalytic activity in total oxidation of ethyl acetate and methanol decomposition to syngas, but this effect is strongly influenced by support composition. The role of structure, texture, surface properties of the obtained materials on their catalytic properties under different catalytic reactions was the main aspect in the study.

Acknowledgments

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Smart superhydrophilic membranes armed with layered components: Adsorption, decomposition, and separation of pollutants

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Keywords: superhydrophilic, membrane, oil/water separation, water purification

Global water resources have been continuously polluted due to industrial progress. Increasingly frequent oil spill accidents as well as oily industrial wastewater discharges have further led to the severe pollution of various water resources. Therefore, oil/water separation has recently become an important issue in scientific research and practical applications. To address abovementioned issues, various types of superhydrophobic/superoleophilic materials, such as metal meshes, sponges, and polymer, have been reported for oil/water separation. Various hierarchical structures with large water contact angles have been proposed for enhancing the separation efficiency or the flux capacity of various oils. However, most efforts have reported methods that focus on the separation itself of oils from oil/water mixtures rather than on the purification of pollutants that remain in the water after the oil/water separation. This situation led us to develop a smart composite membrane for simultaneous oil/water separation and pollutant purification.

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Synthesis of glycerol carbonate from CO_2 and glycerol over Cu-based catalysts

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Keywords: CO_2, glycerol, Cu-based catalyst, glycerol carbonate

As a by-product of biodiesel manufacture, glycerol is available in a great quantity and urgently needs to be transformed to high value-added derivatives The direct conversion of glycerol with CO_2 into glycerol carbonate is very attractive due to converting two wastes into useful chemicals. However, this reaction is limited by thermodynamics. In order to break the thermodynamic limit, the water formed in the reaction of glycerol with CO_2 needs to be removed.

In present work, Cu-based catalysts were used for the synthesis of glycerol carbonate from glycerol and CO_2 in the presence of pyridine-derivatives, which were used as dehydration reagents to remove water and shift the chemical equilibrium to the glycerol carbonate side.

Cu catalysts were prepared by loading Cu metal component on different supports by wet impregnation method. The properties of Cu-based catalysts were characterized by XRD, BET, TEM, XPS, CO_2-TPD, H_2-TPR, Raman spectra and TG-DTA. The catalytic reaction of glycerol with CO_2 was carried out at a high-pressure autoclave in the presence of a dehydrating agent. Cu-La_2O_3 and Cu-Mn catalysts exhibited high catalytic activity for the formation of glycerol carbonate in the presence of dehydrating agent (CH_3CN) under mild reaction conditions. The carbonylation of glycerol was influenced by the particle size, acidic-basic and redox properties of the catalysts. The effects of different types of dehydrating agent and solvent were also studied. The characterization results suggested that the sizes and basic sites on Cu catalysts had significant effect on the conversion and selectivity in the carbonylation of glycerol. The dehydrating agent (acetonitrile) contributed to the increase of glycerol conversion and the yield of glycerol carbonate. The addition of Mn into Cu catalysts could improve the catalytic performance for increasing the selectivity of glycerol carbonate. Over Cu-La_2O_3 catalyst, the conversion of glycerol and the selectivity to glycerol carbonate were 33.4% and 45.4%, respectively (150 ^{o}C, 7.0 MPa, 12 h).

Acknowledgments

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Acid-modified phonolite and foamed zeolite as supports for NiW catalysts for deoxygenation of waste rendering fat

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Keywords: HDO, fat, phonolite, foam, zeolite

Acid-modified phonolite material (synthesized according to [1]), Al_2O_3/foam zeolite and foam zeolite were used as catalyst supports for NiW catalysts with various Ni/W weight ratios. The zeolite type materials were prepared by a novel procedure from natural clinoptilolite. Phonolite materials were loaded with 15 °wt. % of NiW phase with Ni:W ratios 0.5, 1.0 and 2.0. Al_2O_3/foam zeolite was loaded with 35 wt. % of NiW with Ni:W = 0.30 and pure foamed zeolite was loaded with 43 wt.% of NiW phase with Ni:W = 0.30. Catalysts properties were compared in deoxygenation of rendering fat into hydrocarbons. A reference NiW/Al_2O_3 catalyst (32 % NiW, Ni:W = 0,28) was used for comparison of catalytic properties of synthesized materials. Catalytic tests were carried out in an autoclave pressurized at 7 MPa (H_2) at room temperature. Then, it was hermetically closed and heated to 365 °C for 1 h under vigorous stirring. Catalysts were characterized by N_2 physisorption, XRD and XRF. Waste animal rendering fat was used as feedstock. The liquid products were analysed by simulated distillation, C, H, N, S elemental analysis, ATR and density (15 °C). Gaseous product was characterized by RGA-GC. Thus, the yields to different products such as free fatty acids or hydrocarbons were obtained. Phonolite modified solids were tested the first time as catalysts and compared to classical NiW/Al_2O_3 and novel NiW/foam zeolite type materials.

Figures

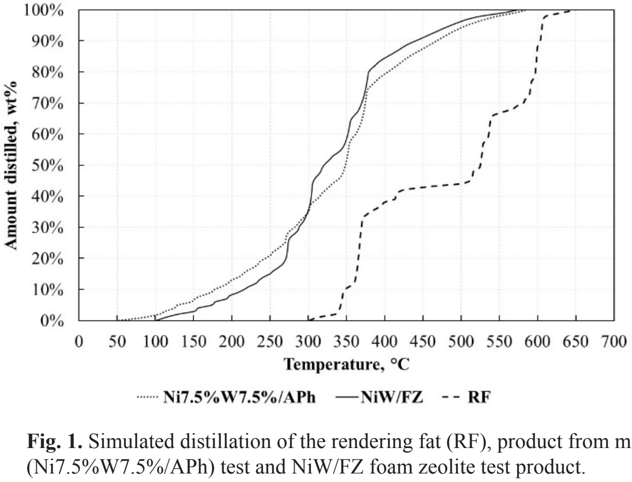

Fig. 1. Simulated distillation of the rendering fat (RF), product from modified phonolite (Ni7.5%W7.5%/APh) test and NiW/FZ foam zeolite test product.

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Preparation and characterization of nanostructured mesoporous Ce-Ti and Ce-Mn oxides and their application as catalysts for environmental protection

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Keywords: Ce-Ti mixed oxides, Ce-Mn mixed oxides, ethyl acetate oxidation

Recently, ceria-based binary materials have been intensively investigated due to their superior oxygen storage capacity and tunable surface properties. These materials show promising application as catalysts in various environmentally feasible processes [1]. The current investigation is focused on the effect of the second metal oxide on the structural, redox and catalytic properties in binary oxides. For the purpose, Ce-Mn and Ce-Ti nanostructured mesoporous oxides with wide variation in their composition were synthesized using template-assisted hydrothermal procedure. The obtained materials were studied by Nitrogen physisorption, X-ray diffraction, X-ray Photoelectronic, Raman, UV–Vis and FTIR spectroscopy as well as temperature-programmed reduction with hydrogen. The contribution of the metal dopant and its amount on the catalytic behaviour of the obtained catalysts in total oxidation of ethyl acetate as a representative VOC was discussed.

Acknowledgments

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Polydopamine-based catalysts with enhanced catalytic activity and stability

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Keywords: polyelectrolyte brush, polydopamine, nanocatalyst, catalytic activity, dye

Three types of surface treatments, namely, polyethyleneimine (PEI) coating, short PEI (S-PEI) grafting, and long PEI (L-PEI) grafting, were performed on polydopamine (Pdop)-based catalysts to enhance their catalytic activity and stability. Brush-grafted catalysts were prepared by the stepwise synthesis of Au and short (or long) PEI brushes on Pdop particles (PdopP/Au/S- or L-PEI grafting). PEI-coated Pdop-based catalysts (PdopP/Au/PEI coating) were also prepared as non-brush-grafted catalysts. Among the surface-treated PdopP/Au catalysts, the brush-grafted catalysts (S-PEI and L-PEI grafting) exhibited excellent and stable catalytic performance because the brush grafting enabled the protection of the catalysts against harsh conditions, effective transfer of reactants to the catalysts, and confinement of reactants around the catalysts. The brush-grafted catalysts could also more effectively decompose larger dyes than the non-brush-grafted catalysts. The process-to-effectiveness of PEI coating is the best because the release of Pdop from PdopP/Au was moderately inhibited by the presence of only one layer of PEI coating on the PdopP/Au. Thus, this approach could be an alternative method to enhance the stability of PdopP/Au catalysts.

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Niobia-supported CoMo hydrodesulfurization catalyst: A kinetic approach

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Keywords: hydrodesulfurization, niobia, sulfide catalyst, nitrilotriacetic acid, CoMo catalyst

Hydrodesulfurization (HDS) is one of the largest heterogeneously catalyzed processes in the present fuel and petrochemical industry. After decades of research and development, the performance (activity, selectivity, price, lifespan, etc.) of sulfide HDS catalysts is at high level. Further improvements on the industrial scale do not seem easy and in fact it is not utterly and acutely needed. Despite that, evaluation of new supports alternative to alumina, for instance: ZrO_2, TiO_2, active carbon or zeolites, is an important topic of recent research into hydrodesulfurization catalysts. Nb_2O_5 was also considered as the support of Mo and Co(Ni)Mo sulfides and also as precursor of the active phase, niobium sulfide.

The activity expressed per unit surface area (mols m^{-2} s^{-1}), coded as A(m^2) of Nb_2O_5-supported Mo and Co(Ni)Mo catalysts reported in the literature is comparable or even better than that of Al_2O_3-supported catalysts. This result becomes important when one tries to develop high surface area (m^2 g^{-1}) supported-Nb_2O_5 catalysts but keeping the same site reactivity as the one obtained with the low surface area Nb_2O_5 support. On the other hand, for practical applications, the activity per gram basis (mols g^{-1} s^{-1}) coded as A(g) is that of concern. Surface area, S(BET), of Nb_2O_5-supported catalysts was always much lower than that of Al_2O_3-supported catalysts, and the relative activity A(g) of Nb_2O_5 to Al_2O_3-supported Mo and Co(Ni)Mo catalysts is typically reported to be very low, only about 0.1 to 0.3.

A sulfide CoMo/Nb_2O_5 HDS catalyst was successfully and newly prepared using nitrilotriacetic acid (NTA) as complexing agent, where the impregnation solution consisted of NTA, cobalt carbonate and ammonium heptamolybdate. It contained neither NH_4OH nor NO^{3-} auxiliary ions, which is a practical advantage of this green chemistry approach. The hydrodesulfurization activity of the catalyst was tested using thiophene model sulfur compound at 1.0 MPa and 400 °C. The ratio of activities (based on pseudo-first order kinetics) expressed in terms of the rate constant k, where the latter was estimated from specific reaction rate data per mass of catalyst, for the NTA-CoMo/Nb_2O_5 and CoMo/Nb_2O_5 catalysts was found to be 6.6. Thus, using NTA shifted CoMo/Nb_2O_5 system from a low activity catalyst (as observed in the literature) to a high activity catalyst worthwhile for further investigations (present results). The NTA-CoMo/Nb_2O_5 (S(BET) = 40 m^2 g^{-1}) was more active than commercial CoMo/Al_2O_3 (S(BET) = 194 m^2 g^{-1}) not only in terms of specific activity normalized per total surface area (A(m^2), mols m^{-2} s^{-1}, 5.7 times larger) but also in terms of specific activity normalized per mass of catalyst sample (A(g), mols g^{-1} s^{-1}, 1.2 times larger). The results suggest that the combination of two phenomena, the positive effect of NTA in the preparation of supported niobia catalysts and the high A(m^2) activity of CoMo/Nb_2O_5 HDS catalysts, has great potential for the synthesis of very active CoMo/Nb_2O_5 hydrodesulfurization catalysts.

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Comparison of supported cobalt based catalysts with unsupported pellets by mathematical model of full scale catalytic reactor for N_2O abatement in waste gas from HNO_3 production

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Keywords: N_2O, catalytic decomposition, supported catalyst, shaped catalyst, open-cell foam, model

Nitrous oxide is considered as an important pollutant contributing to the greenhouse effect. The largest industrial sources of N_2O emissions are waste gases from nitric acid production plants (globally 400 kt N_2O per year) [1]. Low-temperature catalytic decomposition of N_2O (up to 450 °C) to nitrogen and oxygen offers an attractive solution for decreasing of N_2O emissions in tail gas from nitric acid production plants. Adding of a catalytic reactor for N_2O catalytic decomposition can be applied to existing technologies; the advantage is that the process does not require a reducing agent.

An important question is to choose a suitable catalyst system. This catalyst must be sufficiently active, stable, little sensitive to the action of inhibitory components, which are present in waste gases together with N_2O (usually O_2, NO_x and H_2O), sufficiently selective and relatively cheap. Usage of supported catalysts allows reducing of needed amount of expensive active components in the catalyst, which lowers their price and can increase mechanical strength of catalyst. Open-cell foams are promising structured supports, which offer remarkable properties such as a large external surface area, a high mechanical strength and a high porosity with resulting low pressure drop.

In this work, supported cobalt based catalysts (cobalt active phase deposited on the pelletized Mg-Al mixed oxide and ceramic open-cell foam) and unsupported commercial pellets with the same chemical composition of active phase were compared by mathematical modeling of the full scale reactor for N_2O abatement in waste gas from HNO_3 production plants to evaluate the catalytic activity in industry conditions.

In the case of supported catalysts, the bigger reactors were modeled in comparison to unsupported catalyst to achieve the same N_2O conversion (80 %) on all catalysts. The ceramic foam catalytic reactor contains many times lower content of cobalt and cesium in comparison to supported pellets and unsupported catalyst and possesses lower pressure drop. This confirms the fact that cobalt active phase deposited on ceramic foam is promising for industrial applications.

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Effect of vanadium content and speciation on activity of VO_x/ZrO_2 catalysts in conversion of ethanol to acetaldehyde

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Keywords: oxidative dehydrogenation, ethanol, acetaldehyde, vanadium, zirconia

Efficient use of bio-feeds is a modern trend aiming low-carbon emission economy. High yielding interconversion of small molecule bio-accessible compounds allows proposing a sustainable alternative to a part of petrochemical industry. One of those simple reactions is the oxidative dehydrogenations (ODH) of alcohols, particularly ethanol, to acetaldehyde. Acetaldehyde is an important intermediate used for the production of various bulk chemicals, including acetic acid, acetic anhydride, ethyl acetate, peracetic acid, butanol, 2-ethylhexanol, pentaerythritol, chlorinated acetaldehydes, glyoxal, alkylamines, pyridines and others. Nowadays, the ethylene oxidation over $PdCl_2$ and $CuCl_2$ catalysts, so called Wacker process, is mainly used for the acetaldehyde production. The acetaldehyde production via the oxidative dehydrogenation (ODH) of ethanol appears to be a promising alternative to the Wacker process. The benefits of the ODH process can be seen in implementation of the bio-based renewable raw materials and to keep ethylene for processes, where it cannot easily be substituted, and to remove some of the Wacker's process negative aspects, such as treatment of large amount of wastewater and separation and disposal of chlorinated hydrocarbons.

Aim of current study is to bring new information about the role of the VO_x surface complexes speciation and zirconia support structure of the VO_x/ZrO_2 based catalysts on activity and selectivity in ethanol ODH to acetaldehyde. For this purpose, the set of catalysts differing in vanadium content and speciation was prepared by impregnation of amorphous ZrO_2 by ammonium metavanadate. Structure and texture of the catalysts as well as nature and properties of surface VO_x complexes were thoroughly investigated by combination of various experimental techniques (XRD, N_2 physisorption, Raman and IR spectroscopy and H_2-TPR) and tested in the ethanol ODH reaction under various experimental conditions differing in reaction temperature and contact times.

Effect of vanadium species distribution and crystallinity of ZrO_2 support on catalytic activity in oxidative dehydrogenation of ethanol to acetaldehyde was analyzed and discussed in a broad context. Comparison of catalytic results with the details on vanadium complexes distribution led to conclusion that catalytic activity of the VO_x/ZrO_2 catalysts is heavily dependent on the nature of surface VO_x complexes and their population. The highest activity exhibit oligomeric (small polymeric) vanadate surface complexes dominating on the surface of the catalysts with vanadium content above half of monolayer capacity. Selectivity to acetaldehyde exceeded 93 %. Monomeric VO_x species exhibit low catalytic activity probably due to slow reoxidation of the active species. Catalysts with vanadium content close to or above monolayer capacity suffer from the presence of vanadium pentoxide and/or zirconium vanadate clusters having low activity mainly due to inaccessibility of significant part of vanadium atoms buried inside the clusters. The highest catalytic activity of the oligomeric VO_x species correlates with the lowest temperature for reduction of VO_x species by hydrogen indicating the high reducibility of these species. Comparison of catalytic behavior of VO_x supported on tetragonal and monoclinic phase of ZrO_2 did not show any differences neither in the activity nor the selectivity of the ethanol ODH reaction. Long-term catalytic experiments showed good stability of the catalysts (stable conversion and selectivity for more than 600 h).

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Hydroconversion of biomass-derived γ-valerolactone to 2-methyl-tetrahydrofuran over Co/SiO_2 catalyst

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Keywords: GVL hydroconversion, GVL bonding to silica, in situ DRIFT spectroscopy

Gamma-valerolactone (GVL) derived from lignocellulosic biomass is considered as sustainable platform chemical, which can be used for production of either energy or carbon-based consumer products [1]. Hydroconversion of GVL may lead to the formation of pentanoic acid (PA) or 2-methyl tetrahydrofuran (2-MTHF) as main product [2, 3]. The selectivity can be steered by catalyst.

The present study concerns the catalytic hydroconversion mechanism of GVL over silica supported cobalt catalyst (Co/SiO_2) by complementary application of in situ Diffuse Reflectance Fourier Transform Spectroscopy (DRIFTS) and quantum chemical calculations.

The hydroconversion reaction was carried out at 200-250 °C, 30 bar total pressure, and WHSV= 1 $g_{GVL}\cdot g_{cat.}^{1}\cdot h^{1}$ using flow-through microreactor. The Co/SiO_2 catalyst was found to contain Co sites having moderate hydrogenating activity and also Lewis acid sites generated by the unreduced fraction of Co species. Product distribution showed that the reaction involves hydrogenation, hydrogenolysis, and dehydration steps, i.e., the Co/SiO_2 catalyst must have two catalytic functions.

At 41 mol % conversion the main products were 2-MTHF (69.5 % selectivity) and pentanols (19.6 % selectivity). The lack of PA in the product mixture suggests that the cleavage of the C-O bond in the GVL ring must have been occurred on the carbonyl side of the molecule.

Analysis of DRIFT spectra and electronic structure calculations suggest that oxygen atoms of GVL establish H-bonds with the silanol groups of the Co/SiO_2 catalyst. Three structures were distinguished by DRIFTS experiment and assigned by calculation. The in situ DRIFT spectroscopic investigation of the GVL hydroconversion showed that conversion weakened most strongly the $\beta_s(CH_2)$ band of the $CH_2(C{=}O)$ group. Bands assigned to other moieties of the GVL molecule were hardly affected. The ester linkage of GVL was found to be activated for hydrogenolysis in the structure wherein both the ring and the carbonyl oxygen were bound to silanol groups. Results strongly suggests that the first step of GVL conversion is the hydrogenation of the C=O group. The reaction proceeds via hydrogenolysis of the neighboring C-O bond of the ring, giving 1,4-pentanediol that is intermediate of 2-MTHF and pentanol formation.

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Kinetics of decalin dehydrogenation on Pt/SiO_2 catalyst for hydrogen production

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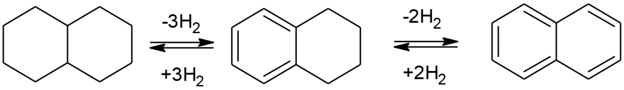
Keywords: catalysis, dehydrogenation, decalin, hydrogen storage, kinetic

At present, the development of hydrogen-based fuel cells is one of the main directions in the development of clean energy sources. One of the major issue for wide application of hydrogen-based energetics is problem of safe storage and distribution of pure hydrogen. The introducing of the method of chemical hydrogen storage based on the hydrogenation-dehydrogenation of liquid organic hydrogen carriers (LOHC) is a perspective way to solve this problem. [1, 2].

Cycloalkanes are promising compounds for hydrogen storage that are able to accumulate 5-7 wt.% of hydrogen. One of the most attractive candidate as LOHC is decalin, since the content of hydrogen in decalin is higher than, for example, in cyclohexane and methylcyclohexane.

The decalin dehydrogenation is consistent and reversible reaction with formation of tetralin as intermediate and naphthalene as product:



The process of decalin dehydrogenation on Pt/SiO_2 catalysts (2 and 6 wt.% of Pt) was considered in this study. Decalin solution in n-heptane (1 wt.%) was used as a model mixture. Synthesized catalysts were characterized by temperature programmed reduction and high-resolution transmission electron microscopy. Catalytic tests were carried out at a fixed-bed flow reactor at temperatures of 300-335 °C, pressure of 0.5 MPa, feed rate of 1-120 h^{-1} and hydrogen:decalin ratio of 440 mol/mol.

Thus, the Pt/SiO_2 catalyst is active in the decalin dehydrogenation/naphthalene hydrogenation reactions in the considered temperature range. It is shown with increasing the metal content in the catalyst the conversion of decalin also increases, all other conditions being equal. The influence of temperature, pressure and volume rate of substrate on the rate constants of direct and reverse reactions were studied, and the kinetic characteristics of the decalin dehydrogenation/naphthalene hydrogenation were obtained. The results could be useful for selection of promising LOHC.

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Selectivity of a biomimetic catalyst in the process of oxidation of cyclohexane by hydrogen peroxide in the mixture with its derivatives

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Keywords: biomimetic, cyclohexane, hydrogen peroxide, heterogeneous

Heterogeneous biomimetic catalysts based on iron-porphyrin complexes have demonstrated high activity and selectivity in the oxidation of a large number of hydrocarbons including oxidation of cyclohexane with hydrogen peroxide [1, 2].

Activity and selectivity of biomimetic catalysts per-FTPhPFe (III) OH / Al_2O_3 and PPFe (III) OH / Al_2O_3 towards particular compound have been studied during the oxidation of cyclohexane.

The study of oxidation of cyclohexane containing 88.85% of C_6H_{12}, 6.25% of $C_6H_{11}OH$ and 2.53% of $CH_3C_6H_{11}$ on per-FTPhPFe (III) OH / Al_2O_3 biomimetic has been carried out at 130–230°C temperature range with the use of 25% aqueous solution of hydrogen peroxide as the oxidant. The results of the study have demonstrated that cyclohexane in the process of oxidation is being converted and the amount of methylcyclohexane in the raw material remains practically unchanged.

In order to confirm the selective action of the iron-porphyrin-containing biomimetic catalyst in the oxidation of complex mixtures cyclohexane with admixture and artificially prepared mixture containing 45.4% of C_6H_{12}, 38.64% of $CH_3C_6H_{11}$ and 1.91% of $C_6H_{11}OH$ have been used as raw materials.

The data given in Table shows the selective effect of the biomimetic towards cyclohexane in the mixture with significant amount of methylcyclohexane.

During the study of the oxidation reaction of the mixture of cyclohexane products with hydrogen peroxide, the ironporphyrin-containing biomimetic catalyst has also demonstrated high selectivity with respect to cyclohexane.

t, ^{0}C	Composition of raw materials, %				Products of monooxygenase reaction, %						conversion, %	O_2 yield in the catalase reaction
	C_6H_{12}	$C_6H_{11}CH_3$	$C_6H_{11}OH$	dimethylcyclohexane	C_6H_{12}	$C_6H_{11}CH_3$	$C_6H_{11}OH$	$C_6H_{11}O$	C_6H_{10}	dimethylcyclohexane		
150	45,439	38,638	1,913	5,479	37,1	38,928	0,641	3,445	6,256	6,771	8,342	91
180	45,439	38,638	1,913	5,479	33,69	39,31	0,448	4,239	8,973	7,078	11,66	88
200	45,439	38,638	1,913	5,479	29,34	36,579	2,793	5,715	9,5	7,165	16,0	84
220	45,439	38,638	1,913	5,479	24,85	38,63	2,5	7,5	12,5	6,7	20,5	79

Results of cyclohexane oxidation in the mixture on PPFe (III) / Al_2O_3 biomimetic with hydrogen peroxide: $[H_2O_2] = 20\%$, $V_{H_2O_2} = 1.41$ ml / h, $V_{C_6H_{12}} = 0.9$ ml / hr.

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The catalytic effect of iron based additives on the efficiency of the selective non catalytic reduction of NO_x by ammonia

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Keywords: SNCR, SCR, nitric oxide, additive, iron oxide, catalytic oxidation

Selective non catalytic reduction of NO_x by ammonia (SNCR) represents worldwide commercially used process for NO_x emissions decrease. The main disadvantage is its relatively low efficiency of 60 %. Therefore, there is an effort to increase the SNCR process efficiency and one possible way is the usage of additives, which are supposed to intensify NO_x reduction process [1]. The use of iron-based additives to reduce NO_x emissions from stationary combustion processes was published by V. Lissianski [2]. The patent [3], which is from the same authors, states that the additive can be added to the main combustion chamber as well as reburning chamber, and that the addition of the metal-based additive to the reburning chamber is effective in the presence of a reducing agent (N-reagent) but also surprisingly even in his absence. Existing research on selective catalytic reduction of NO_x (SCR) on iron oxides focuses predominantly on the temperature range below 500 °C, under conditions where selective catalytic reduction (SCR) by NH_3 is normally used. The influence of Fe and its oxides on NO_x reduction by NH_3 above 500 °C was published only minimally [4], however the understanding of the effect of iron based additives, which are commonly accessible and cheap, at conditions suitable for NSCR can be helpful for the improved application of the SNCR process.

Therefore, the catalytic effect of iron based additives on the efficiency of the selective non catalytic reduction of NO_x by ammonia in the presence of oxygen and water vapor was tested in the fix bed reactor at 700 and 900 °C. It was found out that Fe oxides have inhibitory effect on the SNCR process which can be explained by the ability of the oxides to non-selectively oxidize ammonia into nitrogen or NO_x. The negative effect of additives is reduced with increasing temperature from 700 to 900 °C and with decreasing of oxygen amount in the feed gas and depends of the extent of oxidation degree of the iron oxide.

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DFT study of catalytic reaction kinetics for dimethyl ether synthesis

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Keywords: syngas, Cu-based catalyst, DFT

The Association for the Study of Peak Oil & Gas (ASPO) predicts that the amount of petroleum exploitation will decline in earnest by 2020, and the development and investment of non-traditional resources to reduce dependence on petroleum are being concentrated around the world. With the development of shale gas extraction technology, abundant and inexpensive supply and use of C1 gas is expanding. C1 is a technology that produces a variety of useful chemicals by using one carbon material such as CH_4 and CO. C1 gas is less dependent on crude oil prices, which means that it can replace petrochemicals in every high oil price situation.

This study deals with the process of producing dimethyl ether (DME) from syngas (CO + H2), which is a CO-based gas in C1 gas. DME is a multipurpose fuel that can replace diesel fuel and LPG. DME is also an intermediate of various chemical materials such as methyl acetate, acetic acid and ethanol. Understanding the catalytic reaction mechanism and kinetics from syngas to DME is essential for the design of reactors and processes that produce DME based on C1 gas.

In this study, we focus on the reaction mechanism analysis and kinetic parameter estimation by constructing a sophisticated reaction kinetics model through density functional theory (DFT) for the reaction of DME production from syngas using Cu-based heterogeneous catalyst and solid acid catalysts such as γ-alumina and zeolite. Furthermore, based on the developed reaction kinetics model, a simple catalytic reactor model for this reaction process is constructed to analyze CO conversion, DME yield and selectivity according to reactor conditions.

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Influence of dealumination of MFI-type zeolite on pairing site distribution

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Keywords: zeolite dealumination, MFI

The framework Al atoms in Si-rich zeolites with Si/Al≥12 occur in Al–$(Si)_n$–Al sequences located in one ring (paired sites for n=1 and unpaired sites for n≥2) or in different rings for n≥2 (isolated sites). Isolated and paired sites are characterized by different catalytic properties in different catalytic reactions including oligomerization of light alkenes, decomposition of nitric oxide, MTG reaction etc. The influence of Si and Al sources on Al distribution was determined in [1]. Recently alkali cations were found to be the factor responsible for Al incorporation as isolated sites [2]. Thus, the general approaches of paired/isolated Al sites creation during the synthesis were developed. However the influence of dealumination procedure on pairing sites distribution is still unclear.

In this work we studied the influence of dealumination agent type, its concentration and the temperature of dealumination procedure on Al pairing site distribution in MFI framework. Nitric acid and ammonium hexafluorosilicate (AHFS) in ammonium acetate buffer solution were chosen as the typical dealuminating agents. The commercial CBV-8014 zeolite was used as a starting material for study.

The extensive leaching of paired Al sites was observed in the case of treatment by nitric acid in comparison with isolated ones. Both the amount and the share of paired sites decrease with total aluminum content decrease (see Table 1) indicating the transformation of paired sites into isolated. Wherein the relative loss of paired sites is much more extensive compared to relative loss of total Al content (~5:1) during the dealumination indicating lower stability of paired Al in acidic conditions compared to isolated ones. The degree of leaching grows with the acid concentration and temperature.

In the case of dealumination by AHFS the share of paired sites after treatment strongly affected by the temperature and on AHFS concentration. It was observed that leaching of aluminum atoms does not change the share of paired sites either for low concentration of AHFS (0.05 M) or for low temperature (50 °C). However the increase of both dealumination temperature and AHFS concentration leads to the predominant leaching of paired sites as in the case of acidic treatment.

Table 1. Influence of dealumination of CBV-8014 zeolite on Al sites distribution

Sample	Si/Al	% paired Al	% isolated Al	Loss of paired Al, %	Total loss of Al, %
CBV-8014	43.4	15.8	84.2	-	-
CBV-8014+1.5 M HNO3, 70 ^oC, 24 h	46.8	11.4	88.6	32.9	6.9
CBV-8014+4.5 M HNO3, 70 ^oC, 24 h	49.4	11.2	88.8	37.4	11.8
CBV-8014+4.5 M HNO3, 90 ^oC, 24 h	52	11.0	89.0	42.0	16.7
CBV-8014+0.05 M AHFS, 80 ^oC, 8h	49	15.5	84.5	12.9	11.1
CBV-8014+0.2 M AHFS, 80 ^oC, 8h	54.8	15.6	84.4	59.0	20.3
CBV-8014+0.2 M AHFS, 50 ^oC, 8h	50.5	8.1	91.9	15.0	13.7

Acknowledgments

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Furfural production from dehydration of xylose catalyzed by titanium phosphate in aqueous system

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Keywords: xylose, furfural, dehydration, titanium phosphate

Furfural is a renewable chemical feedstock for valuable chemicals, polymers and furan-based biofuels. In this research, we investigate dehydration of xylose to furfural by using titanium phosphates as acid catalysts The catalysts are synthesized by hydrothermal process from $TiOCl_2.xHCl$ and H_3PO_4 precursors with various $Ti:PO_4^{3-}$ mole ratios and calcined at 500˚C for 6h. They are characterized by several techniques including XRD, N_2 adsorption-desorption, TEM, temperature-programmed desorption of ammonia, FTIR and TGA. From catalytic testing at 170 ˚C in aqueous phase for 6 h, the highest furfural yield and selectivity of 53.7% and 63.0%, respectively are obtained from the catalyst with the $Ti:PO_4^{3-}$ ratio 1:2 and a mass ratio of catalyst:xylose of 1:10.

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The potential application of terminal alkynes as acid homogeneous catalysts

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Keywords: terminal alkynes, homogeneous catalysis, acid catalysis, acetalization, esterification

Terminal alkynes usually find their application in polymer chemistry (e.g. for preparation of special monomers or polyacetylene polymers).[1,2] The idea of application of these compounds as homogeneous catalysts was based on two premises i) the well-known fact, that terminal alkynes contain an acid hydrogen (Brønsted acidity) [3] and ii) the literary resources mentioning the possible application of terminal alkynes as co-catalysts in some organic reactions [4,5].

Eight terminal alkynes, namely phenylacetylene, 3-phenylprop-1-yne, cyclopropylacetylene, 3cyclohexylprop-1-yne, 1-ethynyl-2-fluorobenzene, 2-ethynyl-*α,α,α*-trifluorotoluene, 1,3diethynylbenzene and 1,4-diethynylbenzene, were used as acid catalysts for acetalization of aliphatic aldehydes (C3 – C7) by methanol and esterification of carboxylic acid (acetic, propanoic and benzoic) by *n*-butanol. The acidities of these compounds were determined as pH values measured in the solution of dimethylsulfoxide. The acidities of abovementioned alkynes were related to the catalytic activity. The reaction rate was also tightly connected with the structure of used substrates in both model reactions. With the increasing chain and branching of hydrocarbon chain of substrate the reaction rate significantly decreased, which is consistent with the results available in the literature [6]. Our study proves the possible application of terminal alkynes as homogeneous acid catalysts with good yields of products in acetalization of aliphatic aldehydes (e.g. dimethoxypropane, yield over 70 % (24 h)) and also in esterification of carboxylic acids (e.g. *n*-butyl acetate, yield over 70 % (24 h)).

Acknowledgments

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Preparation and characterization of hollow fiber type catalyst coaded ZSM-5 zeolite for the endothermic reaction of fuel

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Keywords: high-speed aircraft, catalyst, ZSM-5 zeolite, hollow fiber type support, batch reactor

In modern times, as flight speeds have increased due to improvements in aircraft engine performance, engine heat have also increased. Because of air flow with high heat on the engine output site of the aircraft, it is not easy to cool the superheat of the aircraft engine by the simple air cooling method. Due to these problems, a cooling method through endothermic heat is attracted attention by using a fuel that causes an endothermic reaction in a high-speed aircraft. The cooling method through the endothermic reaction is cooled in two ways. The first is physical heat absorption. When the temperature rises, there is a sensible heat that accompanies it. The second is the heat of reaction corresponding to the chemical heat absorption, which absorbs heat during the fuel decomposes. Normally, since the heat sink of the fuel appears at high temperatures, it does not achieve a great efficiency in high-speed aircraft cooling. However, when the catalyst is used, heat sink appears at a low temperature thereby increasing the cooling efficiency. However, when the catalyst is used as a powder, the catalyst enters the engine and damages the engine or the catalyst can deteriorate the performance due to the sintering. In this study, the ZSM-5 zeolite catalyst, which is excellent in the endothermic reaction of fuel, was coated on a hollow ceramic support to solve the problem of disappearance of the catalyst, and the fuel decomposition characteristics of the catalyst in the batch reactor were evaluated. Also micropores characteristic of catalyst were analyzed by BET and the catalyst coating was confirmed by SEM and XRD.

Acknowledgments
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Activity enhancement of Co-SSZ-13 catalysts during CH_4/NO-SCR reaction

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

Selective catalytic reduction of nitric oxide to nitrogen (NO-SCR) is feasible and important method for the elimination of harmful NO_x emission both from mobile and stationary sources. Copper-containing SSZ-13 zeolites are effective, selective, and hydrothermally stable catalysts of the NO-SCR reaction by reducing agent NH_3. However, it would be advantageous to use cheap and abundantly available CH_4 for the reduction instead of NH_3, especially at power plants fuelled by natural gas. Based on our earlier study [1], CoSSZ13 was expected to be a suitable catalyst of the CH_4/NOSCR reaction.

In the present work SSZ-13 zeolite was hydrothermally synthesized according to the method described by Gao et al. [2]. Active cobalt sites were generated in the zeolite using solid state ion exchange method. Unexpectedly, reused catalysts were found significantly more active than the catalysts freshly activated in He flow at 700 °C. Especially those catalysts showed improved activities at temperatures below about 550 °C, which were used already above about 550 °C (Fig. 1). The reaction generates steam giving the catalyst a hydrothermal treatment at the reaction temperature. Interestingly, high-temperature interaction of reactants and catalyst enhanced the $deNO_x$ activity. In order to shed light on the underlying structural reason of the found phenomenon the fresh and used catalyst samples were examined by DR UV-vis and H_2-TPR techniques. Results suggest that new cobalt oxide species were formed within the pores of the zeolite SSZ-13 during hightemperature reaction. The formed oxide promoted the catalytic oxidation of NO to NO_2, which is an important reaction intermediate of the NO-SCR reaction.

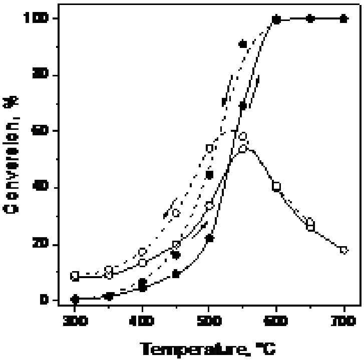

Figure 1. NO (○) and CH_4 (●) conversion over Co-SSZ-13 catalyst. Solid lines: conversion curves obtained at increasing reaction temperatures over the catalyst activated in He at 700 °C. Dashed lines: conversion curves measured at decreasing reaction temperatures after running the NO-SCR reaction at 700°C for 1 h. GHSV = 30000 h^{-1}, reaction mixture: 0.4% NO, 0.4% CH_4, 2.0% O_2 in He.

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Laponite immobilized titania catalysts for photocatalytic degradation of phenols in water

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Keywords: laponite, titania, photocatalysis, phenol degradation

Photocatalytic degradation is an effective and inexpensive process for the elimination of organic pollutants from water. Titana is the most frequently used photocatalyst, however nanosized anatase powder has a tendency to agglomerate, and difficult to recover it from the reaction media. Among others, an effective way of titania immobilization is the preparation of mesoporous composites of titania nanocrystals with silica. Laponite is an ideal candidate as a support for nanosized titania particles because of its peculiar 'house of cards' mesoporous structure and appropriate commercial availability.

Laponite immobilized titania catalysts were prepared by a pillaring process and by hydrothermal synthesis (HT) applying different titania sources ($TiCl_4$ and $TiOSO_4$) (1). Textural investigations (XRD, TEM, N_2 physisorption) evidenced that by the pillaring procedure with titanium chloride a high specific surface area (~450 m^2/g) mesoporous composite with 5-6 nm sized anatase nanoparticles were formed keeping the morphology of parent laponite structure. In contrast, by hydrothermal treatment with titanium oxysulfate the initial laponite structure was destroyed and a more opened nanoporous silica/titania material was formed with bigger (14 nm) anatase particles.

DR UV-Vis spectra of titania/laponite catalyst did not show the so called 'quantumsize effect', i.e. shift of the band gap to higher energy by decreasing particle size. FT-IR spectroscopic investigations revealed the acidic character of hydrothermally prepared sample showing surface sulfate species on titania.

Catalytic activity of titania/laponite composites were tested in photo-oxidation of model compounds of 10^{-5} M phenol and 2,4,6-trichlorophenol water solutions as well as of real waste water. Catalytic tests were carried out in a self-developed batch photo-reactor with oxygen bubbling, applying different wavelengths (185+254 nm, 254 nm, 361 nm) ozone generating and low ozone, low pressure Hg lamps, products of LightTech Co., Hungary. Catalytic results showed that photo-oxidation is more effective than photolysis of phenol compounds. By means of ozone generating lamp phenols could be eliminated in shorter than 5 minutes. Utilization of titania/laponite catalysts (0.1g/L) enhanced the photo-oxidation activity of low ozone lamp (254 nm). Hydrothermally prepared sample showed better catalytic performance than titanium chloride pillared one, comparable to commercial titania nanoparticles. By UVA (361 nm) irradiation the same trend of catalyst efficiency could be detected, probably due to the bigger titania particles and the more opened mesoporous structure of titania/laponite HT catalyst making the catalytically active sites more accessible. Separation of catalysts from reaction media even in tap water was much easier than that of commercial titania, i.e. by self-settling. Degradation of wastewater micro pollutants are also planned to be tested by the developed titania/laponite nanocomposites.

Acknowledgments

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Selective hydrogenation of carboxylic acids and their derivatives over a TiO_2-supported Re (Re/TiO_2) catalyst

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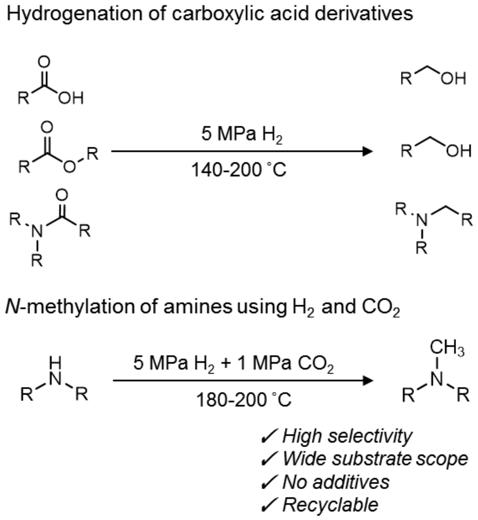
Keywords: rhenium, selective hydrogenation, carboxylic acid derivatives

Reduction of carboxylic acids to form alcohols is a key synthetic transformation for pharmaceutical and fine-chemical industries as well as for biomass conversion.[1] Selective catalytic hydrogenation of carboxylic acids is a straightforward and effective synthetic method. However, the required harsh conditions often lead to low selectivity to desired products. In particular, hydrogenation of aromatic rings occurs rather than hydrogenation of carboxylic acid groups when both moieties are present in substrates. In this study, we propose a versatile heterogeneous catalytic system, comprised of TiO_2-supported Re (Re/TiO_2), which promotes selective alcohol forming hydrogenation reactions of carboxylic acids that contain aromatic and aliphatic moieties, as shown in Scheme 1.[2] Unlike previously-developed catalysts, TiO_2-supported Re has the advantage of being heterogeneous and, therefore, it can be readily recovered and recycled. Moreover, the catalyst is effective for selective hydrogenation of other carboxylic acid derivatives such as esters and amides.[3] The catalyst was also found to promote *N*-methylation of amines with H_2 and CO_2.



Scheme 1. Methods for hydrogenation of carboxylic acids containing aromatic

High-angle annular dark-field scanning TEM (HAADF-STEM) analyses were performed to evaluate the element dispersion and particle size of Re in the Re/TiO_2. The results show that Re is present and that it is highly dispersed over the entirety of the TiO_2 particles. Hydrogenation reactions of 3-phenylpropionic acid were used to screen the properties of various catalysts in the initial phase of this effort. The results of this study show that the Re/TiO_2 produced 3-phenylpropanol and the corresponding ester. On the contrary, low yields of the alcohol and ester were observed when other precious metal (Pt, Ir, Ru, Rh and Pd) containing catalysts were employed. This was caused by competitive formation of products produced via dearomatization of benzene ring. Ag-, Cu-, Ni-, Co-loaded TiO_2 catalysts did not promote the reduction reaction. The yield of 3-phenylpropanol reached 97% after 24 h. It has also been confirmed that the Re/TiO_2 catalyst can catalyze selective hydrogenation of carboxylic acid derivatives such as esters and amides having aromatic rings. In addition, Re/TiO_2 was found to promote *N*-alkylation of amines with carboxylic acids or esters in the presence of H_2. The reaction involves the hydrogenation of carboxylic acids (or esters) to give the corresponding alcohols in the presence of molecular H_2, followed by an *N*-alkylation of the amines with the generated alcohols. Re/TiO_2 also catalyzed the *N*-methylation of various amines in the presence of CO_2 and H_2.

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Indoline and 1-methylindole as a potential Liquid Organic Hydrogen Storage Carrier (LOHC)

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Keywords: LOHC, nitrogen-containing heterocycles, chemical equilibrium, hydrogen energy, hydrogenation, dehydrogenation

In the modern world the development of the energy complex has a stable vector aimed at the use of environmentally friendly and renewable energy sources. One of the promising areas is hydrogen energy. Hydrogen can be obtained by the electrolysis of water using renewable sources of energy - wind, solar and geothermal energy, wave energy, tides, hydropower, biomass, etc. When hydrogen is burned, stored energy is released and water is formed. It is difficult to imagine a more environmentally friendly energy cycle.

The main problem of using hydrogen as an energy source is the method of delivery from the receiving location to the place of consumption. Currently the most cost-effective and safe transportation of hydrogen is via liquid organic carrier hydrogen (LOHC). The most important requirement for LOHC system is the maximum hydrogen capacity during hydrogenation (saturation of the LOHC molecule with hydrogen) and the subsequent dehydrogenation of LOHC with the hydrogen emission and preservation of the chemical purity of the organic molecule LOHC. In this study the main point is determination of the thermodynamic limitations of dehydrogenation reaction of LOHC system while maintaining the selectivity of the process. This report provides a decision for two promising LOHC systems: indoline and 1-methylindole.

The experiment was carried out in a heated autoclave equipped with magnetic stirrer, a sampler, a hydrogen supply system, a resistance thermometer and an electronic pressure sensor. The reaction was conducted in a temperature range of 413-493 K, pressure from 0.1 to 2.6 MPa , hydrogen/LOHC ratio from 0 to 10 mol/mol. Pt, Pd, Ni catalysts supported on SiO2 were used for the reaction. Analysis of the reaction mixture was done with GC, identification of the components was performed by GCMS method.

As a result of experiment the dependencies of equilibrium compositions on temperature, hydrogen ratio and contact time were obtained in such systems as indoline-hydrogen and 1-methylindole-hydrogen. Based on these data, equilibrium constants and thermodynamic characteristics were determined for 6 reactions involving 1-methylindole and 10 reactions involving indoline. Also the conditions of exhaustive hydrogenation of indoline and 1-methylindole and exhaustive dehydrogenation of octahydroindole and 1-methyloctahydroindole have been experimentally determined. It was shown that indoline and 1-methylindole can be used as LOHC systems up to temperatures of 443 and 473 K, respectively. At higher temperatures, the selectivity of the dehydrogenation process is reduced due to hydrogenolysis and compaction reactions.

Acknowledgments

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T2: Catalytic solutions for energy-related challenge

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Enhanced activity and structural stability of CO hydrogenation on phosphorus-modified ordered mesoporous Co_3O_4-Al_2O_3

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Keywords: ordered mesoporous Co_3O_4-Al_2O_3, Fischer-Tropsch synthesis (FTS), phosphorous promoter, hydrophilicity of $AlPO_4$, deactivation

The roles of phosphorus modifier on a highly ordered mesoporous mixed metal oxide of Co_3O_4-Al_2O_3 (m-CoAl), prepared by nanocasting method using KIT-6 as a hard template [1-3], were studied to verify an enhanced activity and structural stability during Fischer-Tropsch synthesis (FTS) reaction. The gradual decrease of FTS activity with time on stream on the pristine m-CoAl was significantly overcome at an optimal amount of phosphorous promoter (0.1–0.3 wt%, P/m-CoAl), which also enhanced a structural stability of the m-CoAl under reductive FTS reaction condition. The partially formed hydrophilic aluminum phosphates on the outer m-CoAl surfaces were responsible for an enhanced activity and structural stability by stabilizing the surface alumina structures and by suppressing wax depositions on a partially formed hydrophilic SiO_2-like tridymite $AlPO_4$ surface in the matrices of the Co_3O_4–Al_2O_3 as shown in Figure 1. Even though the structural stability of the P/m-CoAl during FTS reaction was attributed to a formation of strongly interacted cobalt aluminates ($CoAl_2O_4$), the significant phase segregations of the cobalt and $AlPO_4$ nanoparticles at a larger content of phosphorous promoter above 1wt% were observed due to the much stronger chemical interaction between cobalt and phosphorous species by preferentially forming $AlPO_4$ and $Co_3(PO_4)_2$ phases confirmed by TPR and XAFS analysis on the fresh and used P/m-CoAl (Figure 1), which finally induced the complete structural collapses of the P/m-CoAl.

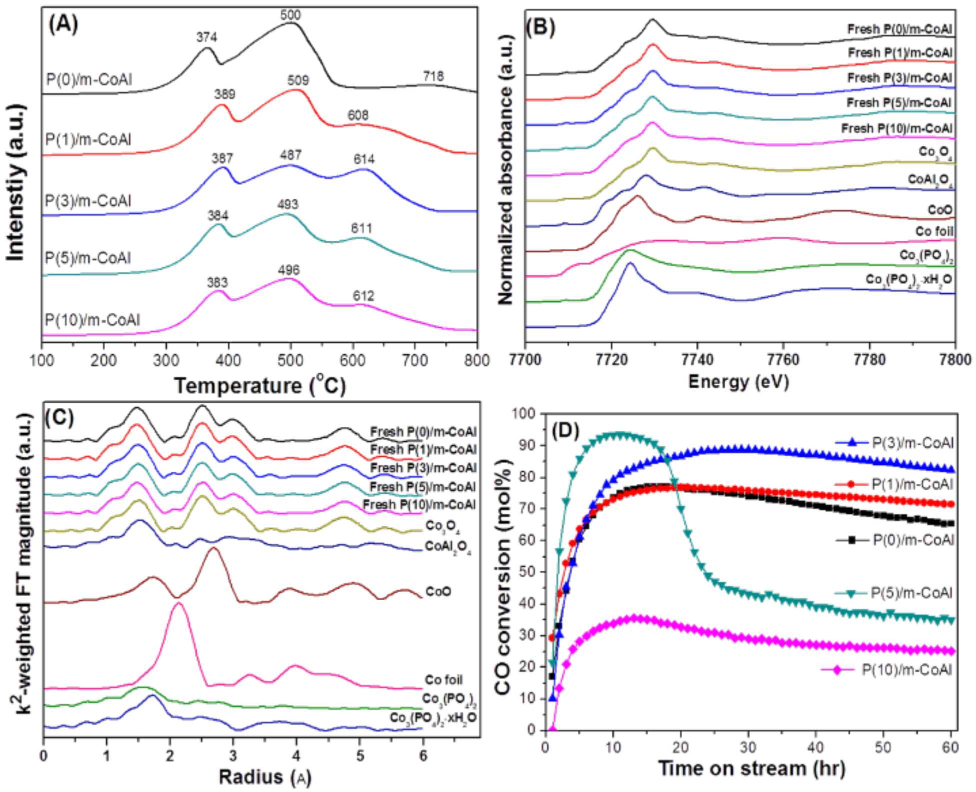

Figure 1/I. (A) TPR patterns of the fresh P/m-CoAl, (B) XANES spectra of the fresh P/m-CoAl with other cobalt references, (C) EXAFS fitting results of the fresh P/m-CoAl with cobalt references, (D) CO conversion with time on stream (TOS, h) on the P/m-CoAl for 60 h on stream

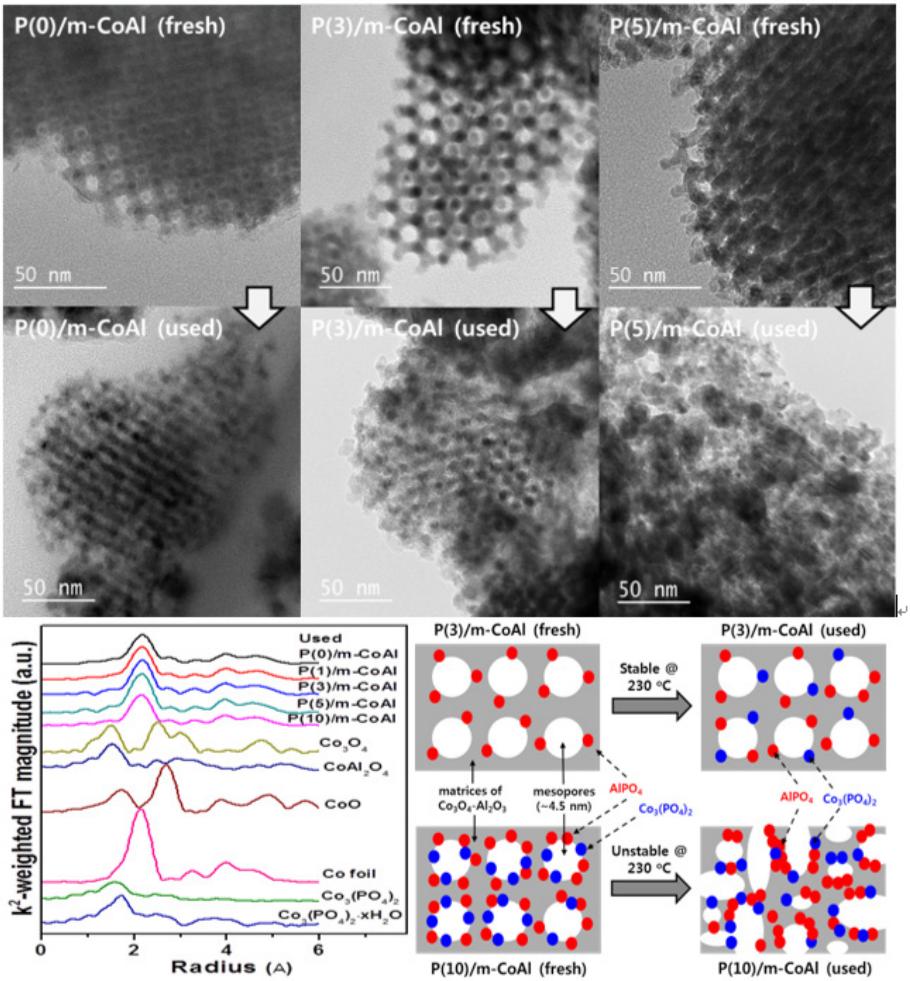

Figure 1/II. TEM images of the fresh and used P/m-CoAl (selected TEM images (upper figures) of the m-CoAl, P(3)/m-CoAl and P(5)/m-CoAl), EXAFFS results of the used P/m-CoAl (lower left-side figure) with the reference cobalt species and schematic diagram (lower right-side figure) of the mesopore collapse mechanisms on the P/m-CoAl

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Fe modified vermiculites dopped with ceria as catalysts for selective catalytic reduction of NOx with NH_3

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Keywords: vermiculites, SCR-NH_3, iron oxide, ceria

Fossil fuels have been the main source of energy for many years, but their burning have negative impact of on the natural environment. During this process CO_2 is formed as well as SO_x and NO_x. Since 2016 the emitted amounts of these gases had to be drastically limited. Effective reduction of toxic components emission can be achieved by subjecting combustion processes to numerous modifications [1-3].

The aim of this work was to determine the activity and selectivity of the obtained catalysts in the selective catalytic reduction of nitrogen oxides using ammonia as a reducing agent (SCR-NH_3). To analyze the structure of the tested catalysts, the infrared absorption spectroscopy using Fourier transform (FTIR) and X-ray diffraction (XRD) were selected.

All analyzed patterns confirmed the structure characteristic of aluminosilicates, to which vermiculite belongs. The VerAlFe3 catalyst was the most selective, with the amount of nitrous oxide in the post-reaction gases being 12 ppm at 150°C. On the other hand, vermiculite modified with 3% iron ions and 0.5% cerium ions showed the best activity, resulting in a conversion of 80%.

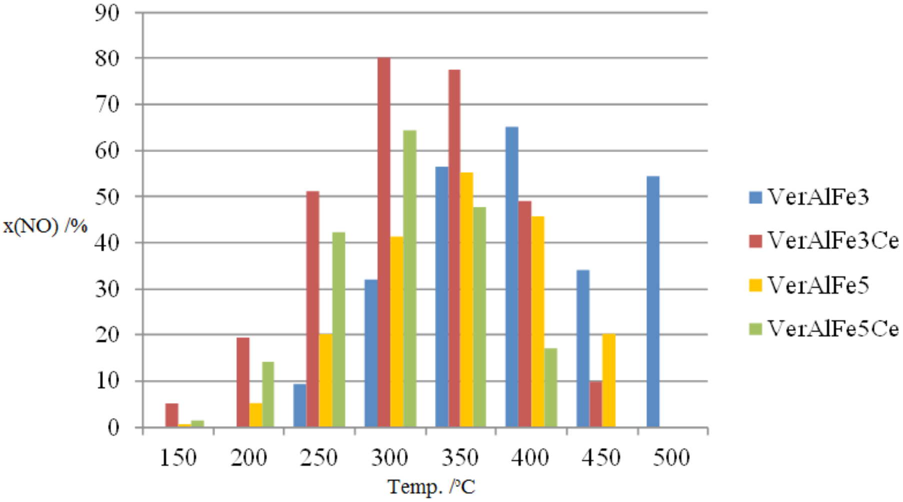

Fig. NO conversion over modified vermiculites

Acknowledgments

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Investigation of Mo-containing Pt-based electrocatalyst with improved CO tolerance for PEM fuel cells

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Keywords: conducting Ti-based mixed oxides, rutile, molybdenum, composite materials, Pt electrocatalysts, CO-tolerance

It has been demonstrated [1] that adding dopants such as Mo to carbon supported Pt catalysts the CO tolerance of hydrogen fueled polymer electrolyte membrane fuel cells (PEMFC) is significantly improved, which has high importance when hydrogen is originated from reformates of biomass derived feedstocks. Mo is reported to (i) provide the necessary OH_{ad} species at less positive potentials than Pt (according to the “bifunctional mechanism”); (ii) modify the electronic structure of Pt and therefore reduce the adsorption strength of CO (the “electronic effect”); and (iii) to increase catalytic activity as the result of the “hydrogen spillover” effect from Pt to molybdenum oxides, leading to formation of hydrogen molybdenum bronze (H_xMoO_3).

In order to suppress leaching of Mo species and simultaneously increase electronic conductivity of a titania matrix our goal was to incorporate Mo into TiO_2 rutile and use this material as support of Pt nanoparticles. The electrochemical properties of novel 20 wt.% Pt electrocatalysts supported on $Ti_{(1-x)}Mo_xO_2$-C (x= 0.2-0.4) composite materials in low-potential CO oxidation reaction (LPCOR) were investigated. The oxidation of CO on the Mo-containing composite supported Pt catalysts commences at exceptionally low potential values (ca. 100 mV). After the weakly bonded CO is oxidized below 400 mV potencial (vs RHE), some hydrogen adsorption can take place indicating that part of the Pt surface is released from adsorbed CO species. Strongly bonded CO still remains on the surface. It has been demonstrated that only CO adsorbed on specific Pt sites, where Pt and Mo atoms are in atomic closeness, can be oxidized below 400 mV potential. The $Ti_{(1-x)}Mo_xO_2$-C catalyst loses its activity in LPCOR when Mo becomes oxidized (above ca. 400 mV). Accordingly, presence of Mo species in lower oxidation state than 6+ is supposed to have crucial role in CO oxidation. Nevertheless, re-reduction of oxidized species formed above 400 mV is strongly hindered when strongly adsorbed carbonyl species are still present. CO_{ad} and surface COOH species can be completely removed only above 550 mV. Oxidized Mo species can be re-reduced and the activity in the LPCOR can be restored if platinum surface is CO free. Clear correlation between the so-called “pre-peak”, the molybdenum redox phenomenon and the CO tolerance of the 20 wt.% Pt $Ti_{(1-x)}Mo_xO_2$-C system was established. Better performance of the Pt/$Ti_{(1-x)}Mo_xO_2$-C electrocatalysts compared to commercially available reference Pt/C and state-of-art CO-tolerant PtRu/C (Quintech) catalysts was also demonstrated.

Acknowledgments

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Poster

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Electrocatalytic performance of NiFe(Co) layered mixed tri-hydroxides on water splitting reaction

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Keywords: electrocatalysis, layered hydroxides, water splitting, materials characterization

Introduction

Production of H_2 and O_2 by water splitting reaction represents an attractive route for clean energy. In this process, oxygen evolution reaction (OER) is the rds due to the slow kinetics which involve multistep proton-coupled electron transfer. Layered mixed di or tri-hydroxides containing 3d transition metals: Ni, Co and Fe have been employed as electrocatalyst in OER in alkaline media. The catalytic reaction involves surface interaction, and for 3d transition metal oxides, it is closely related with the availability of dangling bonds for the metal atoms. Co in NiFe LDH increases the electronic conductivity and the specific surface area but decreases the overpotential and Tafel slopes. It has been demonstrated that the electrocatalytic activity for the OER is closely related to the configuration and cations distribution in the brucite like-layer structure [2]. In this context, specific catalytic site model plays an important role.

Materials and Methods

The NiFe(Co) layered mixed hydroxides were prepared using co-precipitation method at constant pH, varying the Co:Ni ratio. Divalent and trivalent cations ratio was 2. The materials were characterized by techniques XRD, FT-IR, Uv-Vis, EPR, HR-TEM, among others. Electrochemical analyses were carried out, using electrodes prepared by depositing the materials on FTO slide. For electrocatalytic process was used a three-compartment cell coupled in an electrostat-galvanostat.

Results and Discussion

All the obtained solids only contain the peaks and absorption bands characteristics of layered materials detected by XRD and FT-IR. This was also proved by HRTM from the corresponding calculated electron diffraction pattern. The incorporation of cobalt in the NiFe LDH promotes the formation of different active sites for OER, determining the type specially: 1) where one Fe^{3+} atom are surrounded by six M^{2+} ions (M= Co, Ni) labeled FeM_6 site, and 2) the presence of high amount of Fe^{3+} clusters, with Fe_nM_{7-n} (n≤ 2). The oxidation of Co, Ni and/or Fe can occur before the OER stars, in this context, it is complicated to explain however the anodic process when Con Ni and Fe these are in the same structure. Anyway, is well known that redox potential (E_f) associated to the Ni^{2+}/Ni^{3+} faradic process in LDH, is modulated by the presence of accompanying cations.

The contribution of Co is associated to subtract one electron from t_{2g} orbitals present in $Co^{2+}(t_{2g}{}^5e_g{}^2)$, which has one electron unpaired. The profiles in Fig 1A show peaks of Ni^{3+}/Ni^{2+} or Co^{3+}/Co^{2+} redox couple[17]. However, due to the anodic charge (*Qa*) this peak decreases, when the cobalt amount decreases. LSV in the cathodic direction was carried out (Fig 4C) after OER process, one intense peak (*Ec*) was observed, suggesting that during OER other metal sites are oxidized and reduced together with cobalt. OER takes place near to 1.47 V/RHE (Figure 4B), the current density value obtained at 1.57 V/RHE, indicates that electrocatalytic activity towards water splitting follows the tendency: NiCoFe1 > NiCoFe2 >NiCoFe3. At low potential, Tafel plot value was 65 mV dec^{-1}.whereas, at higher potential, the average was near to 110 mV dec^{-1}, indicating that at low overpotential is the rate determining step.

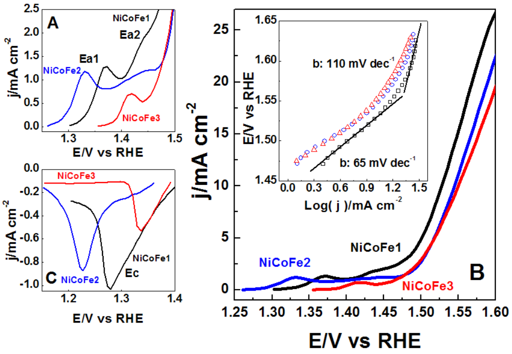

Figure 1. Electrochemical aspects: A) LSV anodic B) performance on OER. Tafel plots. C) LSV cathodic.

Conclusions

The presence of Co in NiFe-based layered catalyst for OER favors the electron-donating facility towards iron cation, which has influence over the Ni catalytic sites. NiCoFe with equimolar ratio composition for the three cations showed the lowest overpotential for OER η< 300 mV, due to the presence of FeM_6 site, where the cobalt is in a low spin configuration, and it can be oxidized at low potential.

Acknowledgments

COFAA and SIP20170776-IPN

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Using of trimetallic NiCoMoS catalysts supported on different carriers for co-hydrotreating of petroleum and renewable fractions

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Keywords: Co-hydrotreating, active phase, NiCoMoS, support, hydrodesulfurization, hydrodeoxygenation, inhibiting effect

Due to the continuous growth of energy consumption in the world, there is much concern about the searching of renewable sources for energy production. In this regard using oils of animal or vegetable origin as a source of hydrocarbon feed looks promising. Economically attractive way of production bio-fuels is co-hydrotreating of petroleum and renewable feed at the refineries without great investments. However, there is a substantial problem of inhibiting of target reactions like hydrodesulfurization (HDS) and hydrogenation (HYD) by oxygen-containing compounds [1]. Recently we obtained the beneficial effect of trimetallic NiCoMoS active phase supported on the alumina in co-hydrotreating of dodecanoic acid, dibenzothiophene (DBT) and naphthalene [2].

The aim of the current research was to investigate the influence of the support on catalytic activity of NiCoMoS catalysts in co-hydrotreating of dodecanoic acid/guaiacol, DBT and naphthalene.

The (Ni)CoMo/*Sup* catalysts (*Sup* = Al_2O_3, SiO_2, SBA-15) were synthesized by wetness impregnation technique with aqueous solutions of $H_6[Co_2Mo_{10}O_{38}H_4]$ (Co_2Mo_{10}-HPA), $NiCO_3$ and citric acid. Catalysts were airdried at 110°C during 5 h and activated by liquid-phase sulfidation at 340°C during 6 h. Synthesized samples were characterized by the following techniques: N_2 adsorption, highly resolution transmission electron microscopy and X-ray photoelectron spectroscopy. Catalytic properties of prepared catalysts were studied in HDS of DBT (2 wt. %), HYD of naphthalene (3 wt. %) and hydrodeoxygenation (HDO) of dodecanoic acid (DA) and guaiacol (Gua) with different concentrations.

It was found that the highest turnover frequency (TOF) value in HDS of DBT showed NiCoMo/SBA-15 catalyst, moreover, the highest HYD/DS selectivity was also obtained at SBA-supported sample. In the case of using DA as inhibiting agent catalysts supported on SBA-15 and Al_2O_3 showed the similar resistance in HDS of DBT though in HYD of naphthalene the most stable catalyst was NiCoMo/Al_2O_3. The similar results were obtained in the case of using Gua as an inhibiting agent – the most stable sample in HDS and HYD reactions was alumina-supported one. At the same time the HDO activity was higher at catalyst supported on SBA-15. The differences in properties of catalysts supported on different carriers can be explained from the position of the optimized morphology of active phase species.

The experiments with diesel hydrotreating and mixture of diesel with plant oil confirmed high effectiveness of trimetallic NiCoMo/Al_2O_3 catalyst for production Euro-5 diesel.

Acknowledgments

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CoW(Mo)/Al_2O_3 hydrotreating catalysts based on mixed Mo-W heteropolyacid: composition, morphology and catalytic properties

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Keywords: hydrotreating, active phase, mixed sulfides, CoMoWS, hydrogenation, hydrodesulfurization, heteropolyanion

The increasing demands for ultra-clean fuels along with severization of environmental requirements for them determine the necessity of the improvement of modern hydrotreating catalysts. It was noted that the use of molybdenum (tungsten) heteropolyacids (HPA) and nickel (cobalt) salts ensures the close spatial arrangements of Co (Ni) and Mo (W) atoms, and thereby leads to the high activity of the sulfide hydrotreating catalysts [1-3]. But there are no works in the literature concerning the use of mixed Mo-W heteropolycompounds as precursors of trimetallic CoWMo hydrotreating catalysts.

The CoW(Mo)/Al_2O_3 catalysts were synthesized by impregnation of the alumina with aqueous solutions of mixed $H_4[SiMo_3W_9O_{40}]$ heteropolyacid (HPA) and cobalt citrate as promotor; with the mechanical mixture of monometallic $SiMo_{12}$HPA and SiW_{12}HPA (Mo/W=9/3)) and cobalt citrate. The reference catalysts based on $SiMo_{12}$HPA and SiW_{12}HPA with equal metal content were also prepared. Synthesized catalysts were characterized using N_2 adsorption, temperature-programmed reduction of H_2, high-resolution transmission electron microscopy, X-ray photoelectron spectroscopy.

Catalytic properties of synthesized samples were investigated in hydrodesulfurization (HDS) of dibenzothiophene (1500 ppm of sulfur), hydrogenation (HYD) of naphthalene (3 wt. %) and hydrodenitrogenation (HDA) of quinoline (0.46 wt. %).

It was found that CoWMo/Al_2O_3 catalyst synthesized from mixed HPA and CoMo/Al_2O_3 sample were characterized with the close activity in all reactions. CoWMo/Al_2O_3 catalyst synthesized from the mechanical mixture of monometallic HPA and CoW/Al_2O_3 sample showed the lowest conversions of model compounds than all synthesized catalysts.

Besides it was found that the stability of CoWMo/Al_2O_3 catalyst synthesized from mixed HPA in HDS and HYD during inhibiting of quinoline was higher than for CoMo/Al_2O_3 and CoWMo/Al_2O_3 sample prepared from the mechanical mixture of monometallic HPA. Thus, using mixed Mo-W HPA for designing hydrotreating catalysts is a promising way.

Acknowledgments

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Modified microspheres as catalysts for selective reduction of NO with ammonia (SCR-NH$_3$)

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Keywords: cenospheres, SCR-NH$_3$, manganese, copper-oxides

Cenospheres are the by-products present in fly ash from the power plants. Cenospheres are gas-filled aluminosilicate spheres, which have many universal properties, and can be used in many fields of industry. The most important properties of the cenospheres are: thermal insulation, good frost resistance or fire resistance. Therefore, there is a growing interest in recovery and the modification of microspheres and their usage in many fields of science and industry [1-3].

The aim of this work was to study the properties of gray and white cenospheres promoted with manganese, iron, copper and nickel ions using IR spectroscopy, X-ray diffraction, scanning electron microscopy and low temperature N$_2$ sorption. New catalysts were also tested in the selective catalytic reduction of NO with ammonia. Obtained results confirmed that modified cenospheres are very promising materials for this process.

The best catalysts modified with copper exhibited about 90% NO conversion at 250^{o}C and small N$_2$O formation. Mn modified cenospheres exhibited the high NO conversion as well but lower selectivity.

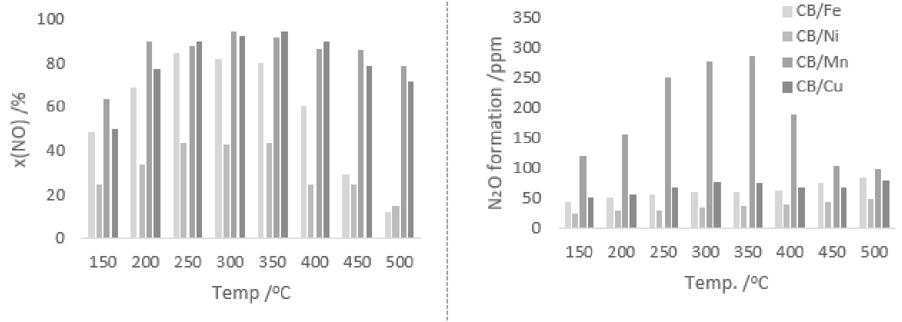

Fig. NO conversion and N2O formation over modified cenospheres.

Acknowledgments

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T3: Polymers and catalysis

Oral

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Polymer cross-metathesis, a new interchain reaction: the kinetics and mechanism of interactions between polynorbornenes and polyoctenamers

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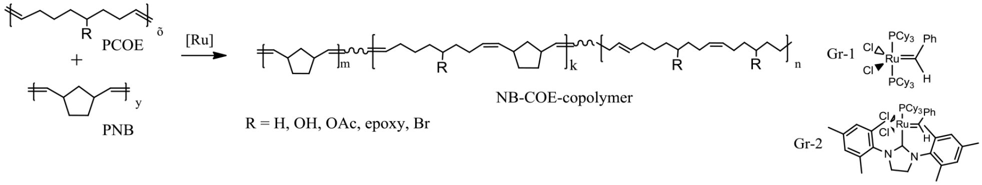
Keywords: Ru-carbene complexes, in situ NMR monitoring, metathesis, Grubbs catalysts

Olefin metathesis is a fast-developing area of polymer chemistry. However, the cross-metathesis between different polymers remained without due scholarly attention for a long time. We have recently studied the cross-metathesis between polynorbornenes (PNBs) and polyoctenamer (PCOE) mediated by the 1st generation Grubbs' catalyst $Cl_2(PCy_3)_2Ru=CHPh$ (Gr-1) with the aim to synthesize a new type of multiblock copolymers which are not available by other ways [1]. We have synthesized for the first time multiblock copolymers of norbornene and cyclooctene, studied the reaction kinetics of PNB with PCOE. By using *in situ* 1H and *ex situ* 13C NMR spectroscopy for monitoring the transformations of Ru-carbene active centers and evolution of the dyad composition in polymer chains, we have gained some insights into the reaction mechanism [2]. In the present study we synthesized new functional NB-COE(R) multiblock copolymers containing HO-, epoxy-, Br, AcO-substituents in COE blocks in the presence of the 1st and 2nd generation Grubbs' catalysts and obtained new information about the kinetics and mechanism of polymer cross-metathesis. Some features introduced by the substituents were revealed. For example, the cross-metathesis in PCOE(OH)/PNB/Gr-2 mixtures was accompanied by a partial hydrogenation of double bonds in the NB-COE(OH) copolymers. 1H NMR spectra demonstrated the formation of Ru-hydride complexes which can mediate the hydrogenation process. The kinetic data analysis made it possible to outline the cross-metathesis scenario for the PNB and PCOE(R) cross-metathesis. At the first stage of the reaction all the initial Ru-benzilydene carbenes of the catalyst were transformed into Ru-PCOE(R) carbenes. PNB-bound carbenes were detected in very low concentrations throughout the whole process thus indicating their higher reactivity, as compared with the PCOE(R)-bound ones. The second stage involving interpolymeric reactions proceeded much slower. The process is controlled by the slowest elementary reaction, which is the interaction between a [Ru]=PCOE carbene and a double C=C bond in a PNB chain. It is hampered, presumably, due to the steric reasons. The influence of substituents in PCOE(R) on the reaction kinetics will be discussed in the presentation.

Figure



Cross-metathesis of polynorbornene and polyoctenamers in the presence of Grubbs' type catalysts

Acknowledgments

The work was supported by the Russian Foundation for Basic Research, project № 16-33-60213

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Novel metal sulfonate polymers as heterogeneous catalyst

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The development of catalysts for heterogeneous systems is in constant expansion, due to their facility of separation by simple filtration as well as the possibility for them to be reused and recycled.

The aim of this work is to evaluate the catalytic activity of cation-containing polymers (Cu^{2+}, Bi^{3+}, In^{3+}, Fe^{2+} or Ca^{2+}) derived from poly(ether ether ketone) (PEEK).

The Friedel-Crafts acylation being an important reaction in organic chemistry, we tested the new polymeric materials for the catalytic acylation of aryl derivatives. A series of aromatic and heteroaromatic ketones was obtained in good yields. The recycling and reuse of the catalysts indicated no loss of activity. The obtained results were correlated with the acylation of aryl derivatives catalysed by several metal tosylate monomers.[1]

We further examined the hydrothiolation of olefins with thioacetic acid as hydrothiolation agent. Compounds including C-S bonds are present in many pharmaceutical, flavor and fragrance products.[2,3] The selected catalyst was an In^{3+}-based polymer sulfonate. The catalyst was prepared by ultrasonic activation of sulfonated PEEK in the presence of indium acetate.

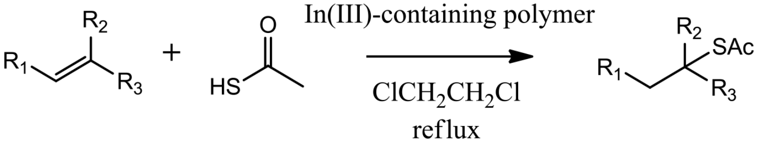

Figure 1. Polymer-catalysed hydrothiolation of olefins with thioacetic acid

The catalytic activity of this polymeric catalyst was compared to that of the corresponding non-polymeric analogues.

A series of thioesters was obtained regioselectively in good yields, in a Markownikov-type addition.

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Poster

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Kinetics of radical polymerization initiated by heterogeneous catalysts including cationic surfactants

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Keywords: catalysis, kinetics, hydroperoxide, styrene, methylmetacrilate, polymerization

Cationic surfactants, particularly quaternary ammonium substances (QUATS), constitute a relatively small part (5-6%) of the total surfactant production. However, they are extremely useful for some specific purposes. Due to the positive charge at neutral pH QUATS adsorbed on negatively charged surfaces of most solid materials, this property is used in the creation of antistatics, corrosion inhibitors, magnetic suspensions, to soften various fabrics, to condition hair and so on. QUATS have antibacterial action, which is indispensable for processing of surgical equipment, the development of disinfectants for household and industrial applications [1,2]. We have found that QUATS form mixed micelles with hydroperoxides (ROOH) in which the accelerated catalytic decomposition of ROOH into free radicals occurs[3].

In this study the kinetics of radical polymerization initiated by mixed micelles {QUATS-ROOH} and by heterogeneous catalysts obtained via adsorption of QUATS on montmorillonite Na and cellulose in combination with hydroperoxides (ROOH). Styrene and methyl methacrylate (MMA) were used as monomers; bromides of cetyltrimethylammonium (CTAB), cetylpiridinium (CPB) and acetylcholine chloride (ACh), which is the most important neurotransmitter that plays an important role in the neuromuscular and cognitive activity of living beings, were used as QUATS in combination with pure cumene hydroperoxide (ROOH). The highest rate of polymerization of both monomers provides a catalyst for cellulose–CTAB. In the more hydrophilic MMA the rate of radical initiation at identical concentrations of the catalyst and the hydroperoxide are much lower than in hydrophobic styrene, however, the rate of polymerization of MMA is higher than in styrene, due to the higher activity of MMA in the reactions of chain growth. Relatively high values of the rate of radical generation upon contact of the cellulose–CTAB and cellulose–ACh, with hydroperoxides open the possibility of creating disinfectants and medical materials on a cellulose basis.

Acknowledgments

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Catalytic reduction of o-nitroaniline in presence of silver nanoparticles loaded composite microgels catalysts

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Keywords: Polymer, microgels, nanoparticles, catalysis, reduction, o-nitro aniline

o-nitro aniline is highly toxic nitro aromatic compound and induces harmful effects when exposed to aquatic system. It can be degraded into o-amino aniline using sodium borohydride reducing agent. Reduction of o-nitro aniline using sodium borohydride reducing agent is thermodynamically feasible reaction but proceeds at very slow rate. Thus, poly(N-isopropylacrylamide-methacrylic acid) [p(nIPm-ac) microgels fabricated with Ag NPs were used as catalyst to speed up the rate of reduction. Prepared hybrid microgels catalyst showed high activity for reduction of o-nitro aniline. Effect of catalyst dose, concentration of NaBH4 and temperature of the medium on value of apparent rate constant for reduction of o-nitro aniline was also studied. Prepared microgels and hybrid microgel particles were characterized by UV vis spectroscopy, Fourier transform infrared spectroscopy and transmission electron microscopy. pH sensitivity of microgel particles was studied by dynamic light scattering analysis. Abrupt change in hydrodynamic radius of microgel particles was observed at pH greater than pka of methacrylic acid.

T4: Producing and utilizing hydrogen

Oral

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Role of the catalyst support in hydrogen production from formic acid over noble metals and MoS_2

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Keywords: formic acid, hydrogen, support effect

Formic acid attracts a lot of attention as it can be used for hydrogen storage and as a hydrogen donor for hydrogenation reactions. Moreover, it can be produced with high yields from biomass using catalysis. There is a need in active, selective and stable catalysts for formic acid decomposition. Our objective was to understand the role of the support for vapor phase decomposition of formic acid over Au catalysts on Al_2O_3, ZrO_2, CeO_2, La_2O_3 and MgO supports, over MoS_2 on graphene flakes [1] and over Pt, Pd and Ru catalysts on N-free and N-doped carbon materials [2,3].

The activity of Au nanoparticles of the same size (2.4-3.0 nm) was strongly dependent on the nature of oxide support. A volcano-type plot on the electronegativity of the support cation was revealed with the Au/Al_2O_3 catalyst on the top (Fig. 1). This catalyst also provided almost CO-free hydrogen production. The observed dependence of the activity was assigned to activation of the formic acid molecule on support sites followed by conversion of the formed intermediate on the Au nanoparticles.

In the case of MoS_2, the role of the graphene flakes was in stabilization of 1 nm - sized MoS_2 clusters with exposed Mo edge sites, which are the active sites of the reaction. Sintering of these clusters at >900 K led to the formation of inactive MoS_2 nanoparticles of 20-30 nm.

The N-doping of the carbon support provided a significant increase of the activity of the supported Pt-group metals (by up to 1 order of magnitude). This was attributed to the formation of new active sites – electron-deficient single metal atoms stabilized by a pair of pyridinic nitrogen atoms located on open edges of graphene fragments. Aberration-corrected HAADF/STEM, CO chemisorption, XPS and DFT studies confirmed this. In summary, the obtained results indicated that the properties of the catalysts in formic acid decomposition can be regulated by variation of the nature of the support.

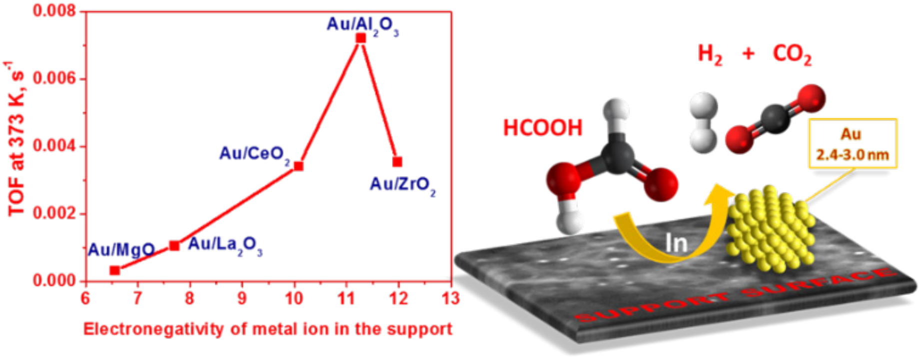

Fig. 1. Dependence of the turnover frequency in formic acid decomposition on the electronegativity of the cation in the support and a scheme of the formic acid molecule interaction with supported Au catalysts.

Acknowledgments

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Effects of preparation method on the properties of cobalt supported ceria catalysts for steam reforming of ethanol

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Keywords: hydrogen production, ethanol steam reforming, cobalt, ceria

With the fossil fuel resource decreasing and the environmental pollution caused by the combustion of fossil fuel, hydrogen energy is considered as a promising future power carriers and prime movers and has attracted more and more attention in many applications all over the world, such as transportation and production of electricity. Currently, hydrogen is mostly produced by methanol and methane, low-temperature ethanol steam reforming could be a well-studied reaction that is of great importance in scientific and commercial applications, because ethanol is the potential for deriving from a biorenewable sources and has the added advantages of low toxicity and being relatively easy to transport and store [1, 2]. The aim of this work was to study the influence of the preparation method on the activity, selectivity and catalyst deactivation of Co/CeO_2 catalysts under steam reforming of ethanol conditions. The catalysts were obtained by co-precipitiation method (denoted as Co/CeO_2_P), hydrothermal method (denoted as Co/CeO2_H), co-precipitation method in the presence of small amount of hydrogen peroxide (denoted as Co/CeO_2_H_2O_2) and co-precipitation method in the presence of surfactant (denoted as Co/CeO_2_S). Characterization of the catalyst was done with XRD, XRF, low-temperature nitrogen adsorption, hydrogen chemisorption, SEM, TEM, thermogravimetric and H_2-TPR methods. The highest BET surface area was obtained for Co/CeO_2_H_2O_2 catalyst whereas Co/CeO_2_P catalyst had the smallest size of cobalt crystallites. The highest ethanol conversion after 21 hours of SRE process ($EtOH/H_2O=1/12$, GHSV=60000 mL/gh, T=420 °C) demonstrates Co/CeO_2_P catalyst but the highest SRE process selectivity to two the most desirable products of reaction, i.e. hydrogen and carbon dioxide was obtained in the presence Co/CeO_2_H_2O_2 catalyst. The large amounts of acetone are produced in the case of all studied catalysts with the exception of Co/CeO_2_H_2O_2 catalyst. On the other hand, there is produced more aldehyde in the presence of this catalyst. Also the production of carbon monoxide is slightly more for this catalyst in comparison with the results obtained for other studied nanomaterials.

Acknowledgments

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Poster

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The effect of impurities on the steam reforming of ethanol over rhodium/alumina

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Introduction

The production of synthesis gas is a key enabler for Fischer-Tropsch synthesis and methanol synthesis. Currently hydrogen and syn-gas are produced principally by steam reforming of methane, however in certain locations the use of biomass may be more cost effective. Steam reforming of bioethanol is a promising route for syn-gas and/or hydrogen production. However, the presence of impurities in bioethanol has the potential to have a significant influence on the activity and lifetime of the catalyst. Therefore, the aim of this project was to study the influence of C_3-impurities (1-propanol, 2-propanol (IPA), propanal, acetone and propylamine) on the steam reforming of ethanol over Rh/Al_2O_3 at 773 K and 20 barg, examining the effect of these impurities on activity, selectivity and catalyst deactivation.

Experimental

Steam reforming of ethanol was performed in a high pressure reactor (20 barg) at 773 K, over 0.2 % $Rh/\alpha\text{-}Al_2O_3$, at 50,000 GHSV. The catalyst (0.25 g) was reduced in flowing hydrogen (50 ml/min) at 873 K for 2 h. After reduction the flow was switched to Ar and the temperature adjusted if necessary. The argon carrier gas and 5:1 water:ethanol mixture were integrated in the vaporizer whose temperature was kept at 773 K. Impurities were added at 1 % relative to ethanol. After exiting the reactor tube the product gases entered a knockout pot (273 K) where high boiling point products were liquefied and collected and analyzed by GC using a Zebron column and FID detector. Gaseous products were analyzed by on-line GC using a TCD detector and a carboxenTm1010 plot column.

Results/Discussion

The addition of a 1 mol.% impurity to the water/ethanol mixture had a significant effect on the conversion of ethanol over the Rh/Al_2O_3 catalyst at 773 K and 20 barg pressure as shown in Figure 1. Table 1 reports the dry gas selectivities, which shows the very clear difference between the effect of acetone and propyl amine compared to that of 1-propanol and IPA. The reaction analysis suggests that both propyl amine and acetone rapidly deactivate the metal component of the catalyst and the residual activity relates to that of the alumina support. Whereas 1-propanol and IPA deactivate the catalyst in general affecting both support and metal in a manner similar to the ethanol.

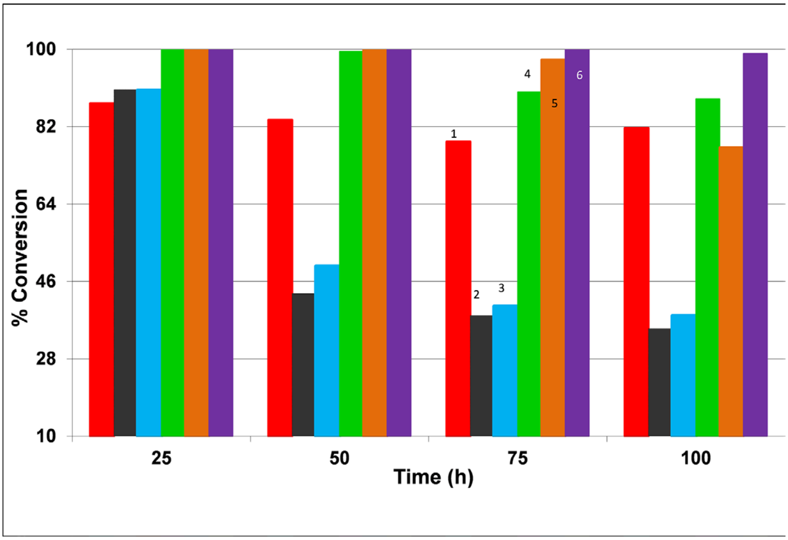

Figure 1. Conversion of ethanol over Rh/Al_2O_3 catalyst during the different impurities reactions. (1= No impurity, 2 = IPA, 3 = 1-propanol, 4 = propanal, 5 = propylamine, 6 = acetone)

The secondary alcohol is more reactive than the primary alcohol with IPA being fully reacted at all TOS. Both propanal and 1-propanol catalyse the formation of carbon nanotubes (CNTs) which are not seen in the absence of the impurities.

Table 1. Dry gas selectivity (%) over Rh/Al_2O_3 in the presence of different impurities

Impurity	**H_2**	**C_2H_4**	**CO_2**	**CO**	**CH_4**	**C_2H_6**
No impurity	64	16	8	4	6	2
1-Propanol	64	14	13	2	5	1
IPA	54	27	10	2	5	1
Propanal	45	0	19	7	29	0
Propylamine	47	1	20	3	28	0
Acetone	44	4	19	5	27	0

Conclusions

The presence of impurities in ethanol has a significant effect on the reaction properties during steam reforming changing activity, selectivity and the nature of carbon deposition. Impurities containing amine and ketone functionalities resulted in rapid poisoning of the metal component of the catalyst.

Acknowledgements

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T5: Basic concepts in catalysis science

Oral

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Bridging the gaps: multiscale analysis of nonlinear behaviors by environmental microscopies

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Non-equilibrium reactions are observed in a variety of reactive systems, including those at the surface of catalytic materials. Probing such reactions and their dynamics during the ongoing processes remains challenging, due to the scarcity of high-resolution techniques allowing for *in situ* experiments. This study reports on the observation and analysis of nonlinear behaviors during the catalytic hydrogenation of NO_2 on Pt catalysts using field emission microscopy (FEM) and environmental scanning electron microscopy (E-SEM). The microscopes run as open reactors, and the dynamics are probed in real-time and during the ongoing reactive processes.

On one hand, FEM enables the study of catalytic reactions taking place at the surface of a nanosized metal tip which acts as a single nanoparticle of catalyst: the reaction can be probed down to 10 nm^2 and at pressures in the 10^{-4} – 10^{-2} Pa range. Different nonlinear behaviors were observed, such as self-sustained periodic oscillations and the propagation of chemical waves as target patterns. On the other hand, the E-SEM instrument allows the study of samples with various morphologies, allowing to approach the complexity of materials encountered in industrial applications. E-SEM can also be used with gas pressures up to tens of Pa. Experiments during the NO_2 hydrogenation were performed on Pt single crystals and on Pt foils, and nonlinear behaviors were observed, mainly in the form of spiral patterns. These patterns were observed on regions as large as 100 μm and over a wide range of pressures: from 10^{-3} to 20 Pa, over four orders of magnitude.

The combination of FEM and E-SEM can be used to observe similar phenomena over different pressure conditions, allowing to bridge the pressure-gap, from 10^{-4} to 20 Pa; but also the materials-gap by analyzing the same reaction on a tip-sample, single crystal and foils corresponding to a mixture of grains of different crystallographic orientations. This also proves the robustness of dissipative, nonlinear behaviors from the mesoscale down to the nanoscale.

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Catalytic reactions imaged at the nanoscale: study of gold-silver alloys by field emission techniques

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Keywords: nanocatalysis, field emission techniques, bimetallic alloys, environmental microscopies

The design of efficient catalysts requires the understanding of the catalytic processes down to the atomic level. Especially, information about the structure of the catalytic surface, the catalytic behaviour of the materials, and their evolution during reaction has to be gleaned. The use of analysis techniques able to observe the surface of catalysts under working conditions is thus needed. A thorough description at the nanoscale remains challenging, especially in the case of bimetallic samples. Field emission techniques such as Field Ion Microscopy (FIM) and Field Emission Microscopy (FEM) are well-suited for studying the structure and reactivity of catalysts: these techniques use samples prepared as sharp tips, the size and shape of which are close to those of a single catalytic nanoparticle. FIM/FEM studies are performed during the ongoing catalytic reactions by real-time imaging and in direct space. The reactions can be studied at temperature up to maximum 1000 K and at pressures ranging from UHV to 10^{-2} Pa.

In this work, FIM is used to characterize the sample with atomic resolution, while FEM is used to study the reaction dynamics. FEM is based on the emission of electrons from the sample, which is affected by the presence of adsorbates. Local variations of the work function are detected in the form of a brightness pattern, and the surface composition of the sample can be qualitatively monitored during the ongoing catalytic reaction. The establishment of a surface structure/reactivity relationship is performed by comparison of micrographs obtained in respectively FIM and FEM modes.

Here, we studied the catalytic activity of Au-Ag samples, which represent a higher level of complexity as compared to single metal samples. The N_2O+H_2 reaction over Au-8.8at.%Ag samples showed a strong dependence of the reaction dynamics on the underlying surface structure. The appearance of a specific FEM pattern in the 300-320 K temperature range illustrates the formation of O(ads) species, a key step for oxidation reactions in Au and Au-based catalysis [1]. These highlight the capacity of field emission techniques to image complex phenomena at the nanoscale. Furthermore, chemical probing of the adsorbate-layer can also be done by one dimensional atom probe (1DAP) where intermediate species can be chemically identified. Chemical probing of the near-surface can be performed by 3D atom probe (3DAP) to analyze the changes in the surface composition due to the reaction and to assess composition/reactivity relationships.

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Interlayer dynamics of active sites of promoted transition metal sulfide catalysts and the mechanisms of hydrodesulfurization and alcohol synthesis

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Keywords: active phase, alcohol synthesis, hydrodesulfurization, quantum chemical calculations, transition metal sulfides

Introduction

A new mechanistic model for molybdenum sulfide catalysts with cobalt and nickel promoters under hydrodesulfurization (HDS) reaction conditions was proposed that includes dynamic migration of sulfur and promoter atoms between adjacent sulfide layers[1,2]. The proposed model provides crucial information for rational design of improved hydrotreating catalysts and selection of preferred catalytic reaction conditions for various types of hydrocarbon feedstock via optimization of the density and ratio of "rapid" and "slow" catalyst active sites (AS). Application of the dynamic model to the investigation of the mechanism of the mixed alcohol synthesis over transition metal sulfide (TMS) catalysts modified by potassium is a purpose of given study.

Results and Discussion

Based on the developed concept of interlayer dynamics of AS, we proposed the substantiation of the key statements of three basic models forming the foundation of the modern concepts about the mechanism of hydroprocessing catalysis by transition metal (Mo, Co) sulfide, and the boundary conditions for the work of these models are presented. The proposed model makes it possible to develop criteria for the estimation of the efficiency of the catalysts used for hydrodesulfurization of raw materials of various types.

The principles were developed for the preparation of efficient sulfide catalysts based on molybdenum promoted with cobalt and modified by potassium for the synthesis of alcohols from syngas. The introduction of potassium substantially modifies the morphology of molybdenum disulfide crystallites, increasing the average number of layers and the average linear sizes of the crystallites. An alkaline metal forms a single phase with molybdenum sulfide and substantially changes its structure. It was assumed that the formation of alcohols and hydrocarbons from CO and H_2 is caused by the formation of AS containing potassium in the active phase of the (Co)MoS catalyst. The mechanism was proposed for the formation of alcohols on the sulfide KCoMoS catalysts. Thus, the application of the interlayer concept as a generalized approach to such different processes as hydroprocessing of various hydrocarbon raw materials and oxygenation makes it possible to explain the experimental structure–properties correlations and to optimize the catalyst composition for these processes. Quantum chemical calculations using the density functional theory (DFT) approach, evidence the potassium influence on CoMoS active sites manifested in the electron density transfer from the potassium atom onto transition metal atoms (predominantly to Co) and in the decrease of the Co atom's electron deficiency. The consequence is Lewis acidity reduction, which, in turn, leads to the decrease of adsorption energies of CO and H_2. Moreover, potassium promotes dissociative adsorption of molecular hydrogen (Fig. 1).

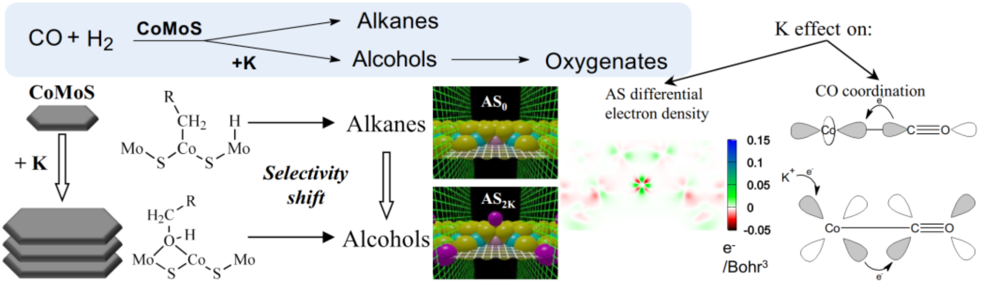

Figure 1. Effect of potassium addition on morphology, electron density of the AS and on the reaction pathways of alcohol formation.

The edge-rim and interlayer dynamic models can be applied for the explanation of KCoMoS catalyst activity in the alcohol synthesis. The active sites responsible for the alcohol formation were attributed to be alkali-modified HDS AS[3,4]. These data have been used to design the mechanism of the synthesis gas conversion over the K-modified CoMoS catalyst. The KCoMoS-based catalysts are expected to be suitable for production of alcohols from synthesis gas.

Conclusions

Application of the interlayer concept as a generalized approach to such different processes as HDS of various hydrocarbon raw materials and synthesis gas conversion into alcohols and other oxygenates makes it possible to explain the experimental structure—properties correlations and to optimize the catalyst composition for these processes.

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Experimental and kinetic modelling studies of the methanol to hydrocarbons reaction over H-ZSM-5 zeolite

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Keywords: deactivation, H-ZSM-5, methanol to hydrocarbons

The methanol to hydrocarbons (MTH) reaction over H-ZSM-5 zeolites has been investigated extensively since its discovery in 1970s and was gaining new scientific and industrial interest in the last two decades [1]. Mechanistic aspects of the reaction attracted most attention with much less interest to the studies of catalyst deactivation (until 2000-2005). Then deactivation and catalyst stability have become the subject of relatively large number of studies (see references in ref. 2). Most of the researchers were focused on the issues related to the catalyst stability and comparison of the time-on-stream (TOS) behaviour of different catalysts, including description of the deactivation by kinetic models [2], but no kinetic studies into the nature of the coking species were reported. This question is however an important one, as many different types of hydrocarbons are formed in the MTH reaction (olefins, aromatics, alkanes), not to forget methanol and dimethylether (DME) that can also contribute to coke formation [3].

This study was undertaken to get insights into the nature of the reaction components of the MTH reaction that are responsible for coking and related catalyst deactivation. Understanding of this matter would allow one to develop a meaningful quantitative description of the deactivation process and, by doing this, to contribute to the development of catalysts with enhanced stability.

To achieve this goal we conducted an experimental study of the methanol transformation into hydrocarbons over H-ZSM-5 zeolite (Si/Al = 34) at 370 ^{o}C and atmospheric pressure (the feed comprised 25 wt% methanol in nitrogen). The experiments were done at different TOS and contact times. Then a kinetic model was constructed to describe, first, the product distribution vs contact time over fresh catalyst, and, second, methanol conversion and product distribution vs TOS. Kinetic modelling of TOS experiments was performed at different initial conversions (15–100%) to ascertain the role of different reaction components in the catalyst deactivation.

The reaction scheme, which formed the basis for the steady state kinetic model, includes (1) the primary steps of olefin formation, (2) olefins formation via olefin cycle, (3) aromatics and alkanes formation, and (4) olefin formation via aromatic cycle. The differential rate equations were integrated using Runge Kutta procedure and quantitative description of the reaction components were obtained as functions of contact time. The change of methanol conversion and product distribution with TOS was modelled next, using different modes of acid sites deactivation.

The comparison of the kinetic modelling and experimental results has demonstrated clearly that olefins act as the major contributors to coke formation.

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Poster

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Fallacies in reaction kinetics

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Keywords: good scientific practice, linearization, activation parameters, isokinetic temperature

Based on three recent publications,[1-3] this poster will list a number of common misconceptions encountered in chemical kinetics. These fallacies often appear even in otherwise high-quality publications and can typically be avoided only through maintaining constant awareness about their possible occurrence. The following specific topics will be covered:

- The fallacy of reaction rates
- The fallacy of activities in rate laws
- The fallacy of turnover frequencies
- The fallacy of rate constants
- The fallacy of the rate coefficients
- The fallacy of consecutive processes
- The fallacy of parallel processes
- The fallacy of rate determining steps
- The fallacy of exchange reactions
- The fallacy of induction periods
- The fallacy of activation energies
- The fallacy of the free energies of activation
- The fallacy of activation entropies
- The fallacy of activation volumes
- The fallacy of isokinetic temperatures
- The fallacy of diffusion limited rate constants
- The fallacy of unimolecular reactions
- The fallacy of termolecular elementary reactions
- The fallacy of radical scavengers
- The fallacy of linearization
- The fallacy of R values
- The fallacy of curve fitting

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Activation of the surface of perovskites of BIZRVOX family by phosphate groups

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The possibility of modification in the perovskite structure of bismuth vanadate $Bi_4(V_{1-x}M_x)_2O_{11-\delta}$ by 3d-metal ions allows their usage as heterogeneous catalysts in the acide–base and redox reactions [1]. The aim of this work is to study the effect of Zr^{4+} cations and PO_4^{3-} anions adsorbed by two way (from vapor phase (1) and from solution (2)) on the surface of bismuth vanadate $Bi_4V_2O_{11-\delta}$ in conversions of isobutanol.

The samples of $Bi_4(V_{1-x}Zr_x)_2O_{11-\delta}$ (x = 0.05, 0.10, 0.15) were obtained by the solid state synthesis, and were characterized by XRD, IR, XPS. Catalytic activity of BIZRVOX was tested under flow conditions with chromatographic analysis of the reaction products. The pyridin adsorption from solutions by spectrophotometric and the dehydration of alcohol were used as chemical probes to measure acid sites.

Acid sites of Brandstad formed by the acid treatment (fig.1). Phosphate groups are associated with zirconium(IV) cation according to IR spectroscopy. The yield of the product depends on the amount of zirconium ions and the type of treatment. Acid solution treatment is 2-3 times more effective than acid vapor treatment: the increase in activity is associated with a decrease in the activation energy of the reaction (fig. 2).

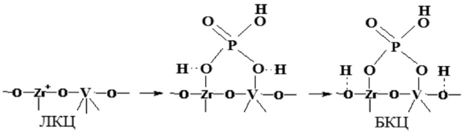

Fig.1. The formation of acid centers

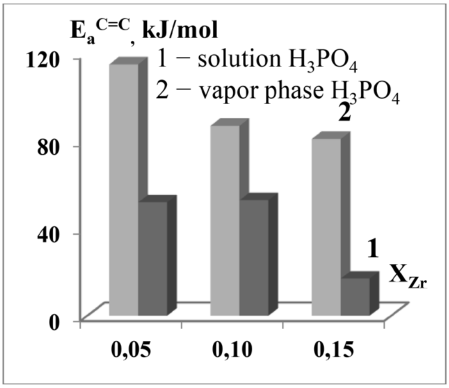

Fig. 2. The activation energy of dehydration of Isobutanol

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T6: Nanoparticle catalysis

Oral

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Effect of medium and nickel salt source in the synthesis of nano-sized nickel catalysts

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Keywords: nickel nano catalysts, hydrazine reduction, characterization, catalytic activity

The transition metal-catalysed carbon-carbon bond forming reaction by the cross coupling of aryl, vinyl and alkyl electrophiles with organoboranes is the well-known Suzuki-Miyaura cross-coupling reaction. Numerous homogeneous and heterogeneous nickel-catalysed versions of this reaction have been published [1,2]. Our aim was to prepare size-controlled nickel nanoparticles (NPs) from different nickel(II) halide salts by the frequently used hydrazine reduction method [3] and to test them in cross-coupling reactions between haloarenes and arylboronic acids leading to biaryls.

The syntheses were carried out at 25°C, 50°C and 75°C, for 4 h in ethanol, water and the mixture of ethanol/water. The as-prepared nanoparticles were mainly characterized by XRD (X-ray diffractometry). The diffractograms showed typical reflections of face-centered cubic NiNPs in most cases. However, the products were nickel(II) hydroxide under some conditions. The shape and size of nanoparticles were studied by scanning electron and transmission electron microscopies. In addition, the size of aggregates were investigated by the dynamic light scattering technique.

The effect of the reaction parameters for the Suzuki-Miyaura cross-coupling reactions in which the activities of the NiNPs prepared in various ways was investigated widely. The best conditions were ethanol as the solvent, 50°C as the reaction temperature and the reactions were followed by gas chromatography.

Acknowledgment

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Bentonite based nanocatalyst for biodiesel synthesis

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Keywords: bentonite, nano, catalyst, biofuel

The biofuels production has been increased because the price of crude oil consistently raising in recent years, and decreasing greenhouse gas emissions. Biofuels can be produced from renewable sources such as biomass and vegetable oils by transesterification reaction which relies on fine scientific history and commercialized technology. Producing biodiesel would also reduce CO_2 emission. On the other hand, biodiesel proffers momentous environmental advantages such as SOX reduction. More over biodiesel is non-toxic and biodegradable. The significant role of catalyst as a solution to efficient technology is outlined, with some other elements that affect the quality and yield of product including feed stock related effects and different situations. This research investigates nanobentonite catalyst as an efficient and reusable solid catalyst for biofuel production. The benefits of biofuels compared to fossil fuels: environmentally friendly, accessibility of renewable sources, biodegradable and sustainable, without causing damage to the environment. Magnetic nanoparticles (MNPs) are efficient, and have been recently developed as attractive candidate to support catalyst owning to their unique properties such as easy synthesis and functionalization, good stability, high surface area, and low toxicity. The other potential advantage of MNPs is that it can be separated from the reaction medium by an external magnet. Moreover they are accessible from inexpensive materials and can be easily tuned by structural appropriate surface modification The nanobentonite surface functionalization with nanomagnetic particles is bridging the gap between heterogeneous and homogeneous catalysis. In this work bentonite was functionalized by silica- coated magnetic nanoparticles (MNP) to catalyze the esterification reaction of methanol and oil mixture. Utilizing this structure as a catalyst, the reaction rate was accelerated. Functionalized bentonite was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), X-Ray diffraction (XRD) spectroscopy, thermogravimetric analysis (TGA), nuclear magnetic resonance (NMR), and the application of FTIR spectroscopy together with chemometrics for pattern recognition was also investigated. Trans-esterification of canola oil- methanol mixture was catalyzed by nanobentonite as a solid acidic catalyst. Production of biodiesel was successfully carried out by nanocatalyst and the methyl ester product was analyzed analysis by ^{1}HNMR, ^{13}CNMR, and FTIR spectroscopy.

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Effect of support surface treatment of Co/Graphene Fischer-Tropsch catalysts

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Keywords: cobalt, graphene, Fischer-Tropsch synthesis, catalyst

The supported cobalt catalysts on graphene and surface pretreatment graphene materials are prepared by incipient wetness impregnation method. The graphene have been pretreated by nitric acid, phosphoric acid and sulfuric acid. The structure and reduction properties of the catalysts are investigated by a series of characterization techniques. And the catalytic performance were investigated by continuous stirred tank reactor.

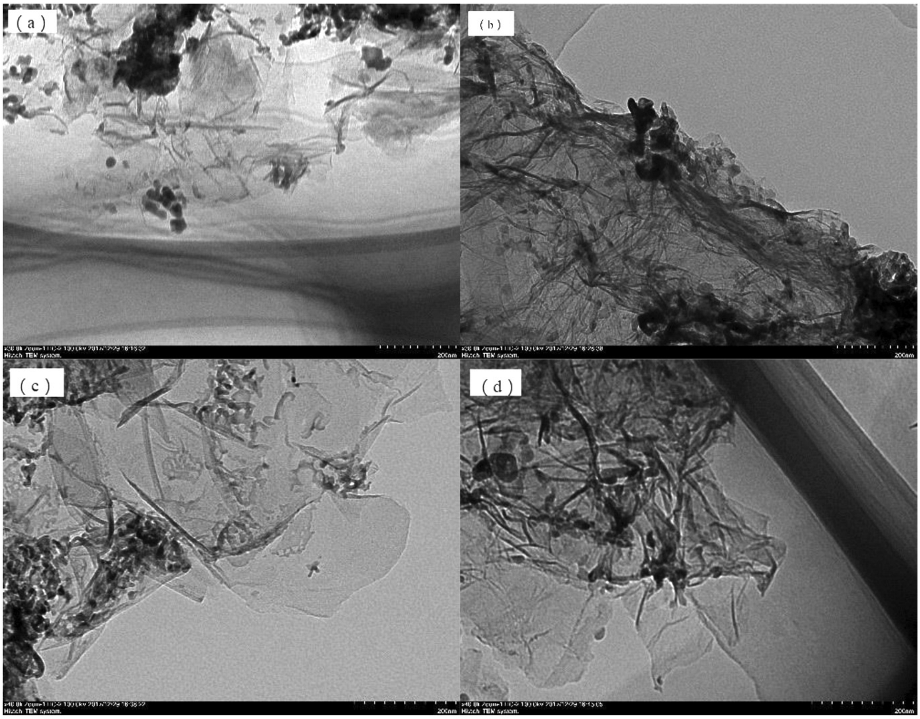

Figure 1. TEM images of different catalysts

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Recovery of TiO_2 substrates using solar-like radiation for photocatalytic applications

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Keywords: titanium dioxide, photocatalytic degradation, azo dyes, Direct Blue 1, catalyst recovery

Currently, there is a concern about environmental issues worldwide. The pollution of water resources due to industrial activities is threatening the availability of drinking water. Therefore, simple and cheap wastewater treatments should be implemented in order to ensure that industrial effluents do not affect the quality of water bodies. Advanced Oxidation Processes (AOPs) have been considered for the degradation of industrial pollutants. Among AOPs, Heterogeneous photocatalysis using TiO_2 has been deeply studied. It is an accepted fact that the capability of TiO_2 to degrade organic pollutants is supported by the adsorption at an earlier stage [1]. However, for pollutants like synthetic dyes, adsorption can decrease the effectiveness of the photocatalysis since dyes can interfere (by blocking) in the absorption of photons by the catalyst surface [2]. As consequence, recovery methods of the photocatalyst should be explored. In this work, a recovery method of the immobilized TiO_2 catalyst using a lamp that mimics solar radiation was studied. Nanoparticulate TiO_2 was immobilized onto a glass fiber-silicone substrate which was used to treat aqueous solutions of an azo dye, Direct Blue 1 (DB1). The photocatalytic treatment using UVC radiation was carried out in a lab scale batch system, as reported previously [2]. A recovery process was applied to the substrate after ten batch treatments. This recovery process consisted on the exposition of the substrate to solar-like radiation for 80 min. Then, the efficiency of the recovery was tested in terms of dye degradation in subsequent batch treatments. As shown in Figure 1a, the removal of DB1 decreased after each batch treatment and the same happened for the recovered substrates. With the recovery process, the degradation capability of the substrate for a first batch treatment was almost restored. However, subsequent batch treatments showed a slight decrease in the degradation up to the fourth batch (Figure 1b). These results suggest that TiO_2 substrates could be recovered by a simple exposition to natural solar radiation.

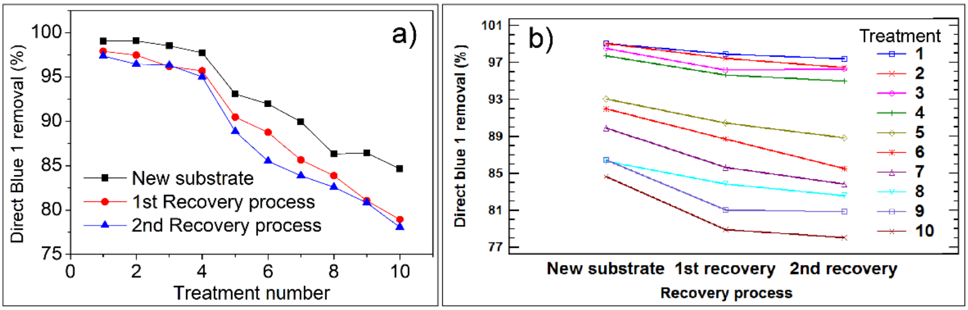

Figure 1. a) DB1 removal after each treatment using the new and recovered substrates b) Interaction plot of the recovery process and treatment number

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Mechanochemically modified hydrazine reduction method for the synthesis of nickel nanoparticles and their catalytic activities

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Keywords: Ni nanoparticles, mechanochemistry, characterization, catalysis

Nowadays, nanoparticles (NPs) of nearly any kind have gained remarkable attention in electrical, optical, physical, and chemical applications due to their unique properties derived from their increased surface to bulk atomic ratios [1,2]. Several techniques were developed to fine-tune this attribute, among others via controlling the size and the shape of NPs. For their syntheses, chemical reduction is a commonly applied method, when a strong reducing agent is used to generate NPs from the dissolved metal salts.

In our synthetic approach, hydrazine mixed in ethanol was used to directly react with nickel hydroxide, which is frequently an intermediate component in the hydrazine reduction route. The $Ni(OH)_2$ particles were pre-milled in a mixer mill, where the transmitted energy was not sufficient to dehydrate the hydroxides, but the frittering effect of milling resulted in significant decrease in the average size of the particles creating reactive defects on their surfaces. In order to explore the potential of this technique, the duration of mechanical treatment was varied systematically in a wide range at fixed, 12 Hz grinding frequency.

The obtained nanoparticles were characterized mainly by X-ray diffractometry, but dynamic light scattering, scanning and transmission electron microscopy measurements were also applied to study the influence of the mechanical treatment on the size, the aggregation tendency and the morphology of NPs. Finally, the catalytic activities of the nanoparticles obtained in various ways were tested in the cross-coupling reaction of aryl halide and arylboronic acid, the Suzuki-Miyaura reaction [3].

Acknowledgment

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DFT study of CO oxidation on ligand-protected gold nanoclusters

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Keywords: active site, mechanism, Au_n, cluster, O_2, CO, quantum chemistry

Thiolate-protected gold nanoclusters (or thiolated Au NCs) have attracted significant interest due to extraordinary properties and beneficial applications in different fields including catalysis [1,2]. Because the atomic composition and structure of thiolated Au NCs are known by DFT and X-ray studies, catalytic properties of such objects including activity, selectivity or stability can be associated with their structure and composition. This fact opens chance to understand the nature of active site of gold nanoparticles in different reactions.

Quantum chemical simulation of catalytic processes involving the thiolated Au NCs has great prospect and provides new thermodynamic and kinetic data, as well as theoretical information concerning the ligand effect and the mechanism of reaction at atomic level. Here we present the results of calculation of $Au_{20}(SR)_{16}$ ($R=CH_3$, Ph) in gas phase, solution and supported on CeO_x (Fig. 1). Different types of cluster's activation at heating were considered. The O_2 and CO adsorption on the cluster, and CO oxidation was simulated. Spin–polarized DFT/PBE level in the scalar–relativistic approach was used.

The method has been tested in details in respect to predict structure and electronic properties of thiolate-protected gold nanoclusters [3, 4]. We propose new insights to the choice of the most appropriate method and perform detail calculation of geometric data and binding energies of Au_2, AuS, and $[(AuSR)_4]_2$. Available experimental data and high-level *ab initio* methods were used as benchmark for assessing the performance of exchange-correlation functionals. The SVWN5, TPSS+D3, PBE96+D3, and PBE0+D3 were found to give the most reliable results and can be recommended for calculation of the structure and properties of thiolate-protected gold clusters. Using TPSS+D3, the reactivity of cyclic $(AuSCH_3)_x$ complexes (x=4-6) in dimerization, Au atom or ion addition, oxidation by O_2 were predicted. Among dimeric complexes, $[(AuSCH_3)_5]_2$ and $[(AuSCH_3)_6]_2$ are the most stable due to special geometrical and electronic structures. The $[Au(AuSCH_3)_5]^+$ and $[Au(AuSCH_3)_6]$ are predicted to be possible intermediates of Au nanocluster growth.

The five isomers of $Au_{20}(SR)_{16}$ ($R=CH_3$, Ph) have been calculated. The Au_7 cluster's core consists of two tetrahedrons united by a common vertex; it is protected by an octameric ring, one triple and two monomeric staple motifs $SR(AuSR)_x$.

The cluster can catalyzed CO oxidation, but the activation energies of the corresponding steps calculated for the fragments: $Au_2(SR)_3^-$, $(AuSR)_4$, $Au(AuSR)_4$, PPh_3AuCH_3 are less than for the clusters. This suggests that the atomic fragments of the ligand-protected gold clusters can be involved in catalytic reaction.

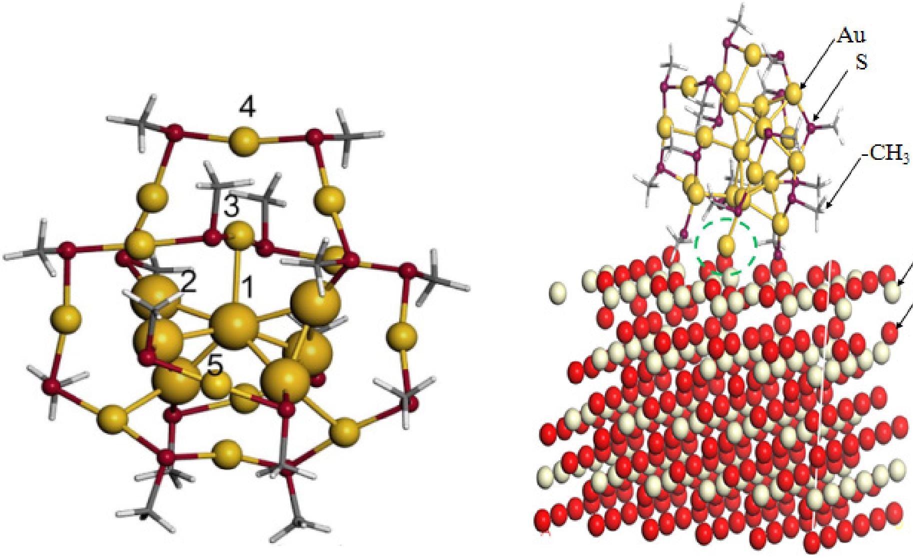

Figure 1. The structure of $Au_{20}(SR)_{16}$ in gas phase and on CeO_x surface.

Acknowledgments

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Poster

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Application of ultrasound irradiation in the syntheses of nickel nanocatalysts

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Keywords: nickel nanoparticles, ultrasound irradiation, characterization, catalytic reactivity

One of the most important applications of sonochemistry is connected to the field of synthesis and modification of inorganic materials [1]. The ultrasound irradiation can enhance the chemical reactivity in the treated materials like the mechanochemical methods do, by tearing out atoms from the bulk surface [2]. Furthermore, the use of ultrasound irradiation could reduce the aggregation facilitating close to monodisperse system [3]. Therefore, the aim of this work was to prepare nickel nanoparticles (NiNPs) without surfactant agent and prevent the aggregation by applying ultrasound irradiation.

The NiNPs could be prepared by hydrazine reduction under wet chemical conditions; and in some cases, the preparation of NiNPs have already been aided with ultrasound irradiation. However, in these articles, merely the effect of reaction time was investigated [4,5]. In our study, nickel iodide was mixed with hydrazine to prepare NiNPs under ultrasound irradiation with different pulse character, power and reaction temperature. The obtained nanoparticles were characterized by XRD (X-ray diffractometry), scanning electron microscopy, dynamic light scattering, energy-dispersive X-ray analysis and transmission electron microscopy.

The powder XRD diffractograms showed typical of face-centered cubic NiNPs. The size and dispersion of the aggregates were altered in a wide range depending on the parameters of the characteristics of the ultrasound irradiation applied. Finally, the catalytic reactivities of the nanoparticles synthesized by ultrasound irradiation and the commonly used magnetic stirring were tested and compared.

Acknowledgment
This work was supported via the grant GINOP-2.3.2-15-2016-00013. The financial help is highly appreciated.

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Nanoparticle catalysts comprising immiscible elements for direct H_2O_2 synthesis: A joint theory-experiment study

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

High-performance catalysts for the direct synthesis of hydrogen peroxide (H_2O_2) mostly utilize costly palladium (Pd), which makes the process commercially less viable. It is imperative to discover an inexpensive alternative. Here, we propose and demonstrate a new catalyst design strategy using nanoparticles (NPs) comprising immiscible elements. As a result, four novel H2O2-producing catalysts (i.e., RhAg, RhAu, PtAu, and IrAg NPs) were developed. In particular, Rh10Ag90, owing to its high Ag content, exhibits a 7.3-fold enhancement in the cost-to-productivity ratio compared to that of prototypic Pd; it may serve as an economical option. Using combinations of ab initio computations and experimental spectroscopies, we demonstrate that the observed productivities of these NPs are a result of the synergy between the two elemental domains at the interface. Our work stands in contrast to the traditional view that Pd is an essential component for efficient H2O2 productions, and thus will substantially increase the scope of future explorations of improved catalyst materials.

Acknowledgments

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Bimetallic nanoparticle catalysts for direct H_2O_2 synthesis

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Keywords: direct H_2O_2 synthesis, bimetallic catalysts, nanoparticles

Direct H_2O_2 synthesis from H_2 and O_2 possesses huge economic potential, since only dilute aqueous solutions are necessary for many applications. In this reason, many researchers are engaged in making an improvement in the direct H_2O_2 synthesis. Palladium is widely known as a key element of catalysts for the direct H_2O_2 synthesis. Palladium, itself, shows quite good catalytic activities. Not a few attempts to improving catalytic activities by alloying Pd with other elements have been reported so far.

In our research, we suggest a new strategy to develop the direct H_2O_2 synthesis catalysts avoiding expensive palladium. In our catalysts, bimetallic catalysts have two domains in one nanoparticle, which carry out two different functions with synergy. One domain participates in dissociation of H_2 and supply of hydrogen atoms, while the other domain takes part in supply of O_2 suppressing O_2 dissociation. In this way, new bimetallic catalysts are realized showing comparable catalytic activities with palladium.

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Detailed kinetic analysis of a simple two-step nanoparticle growth model

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Keywords: average size, time dependence, nucleation, growth, analytical solution

Nanoparticles have found widespread applications in modern chemistry primarily as catalysts of different processes. When nanoparticles are characterized, it is quite customary to measure their size distribution in experimental studies because this property is often highly important for the practical applications. Furthermore, sometimes the formation of nanoparticles is monitored in time, so the distribution (or at least some average size) is often available as a function of time.

In this work, we have postulated a general nucleation-growth model for nanoparticles starting from two earlier models.[1,2] The model consist of a nucleation step, in which two monomer units (A_1) come together to form a dimer nucleus (A_2), and a growth step, in which A_1 is added to a nucleus already containing *i* monomeric units (A_i) and the size of the nucleus increases by on (A_{i+1}).

$$\begin{aligned} &2\mathrm{A}_1 \xrightarrow{k_\mathrm{n}} \mathrm{A}_2 \\ &\mathrm{A}_i + \mathrm{A}_1 \xrightarrow{k_{\mathrm{g},i}} \mathrm{A}_{i+1} \qquad i \geq 2 \end{aligned} \tag{1}$$

Different variants of the model are obtained by giving the connection between growth rate constant $k_{\mathrm{g},i}$ and the size of the nucleus (*i*). A natural such connection is when the growth rate constant is proportional to the number of monomeric units in the nucleus ($k_{\mathrm{g},i} = ik_{\mathrm{g},}$), whilst another reasonable choice is when the growth rate constant is proportional to the surface of the nucleus ($k_{\mathrm{g},i} = i^{2/3}k_{\mathrm{g},}$).

Standard kinetic tools[3,4] were used to derive analytical formulas for the concentrations of the individual species in these models. It was found that analytical formulas were relatively easily found for the case $k_{\mathrm{g},i} = ik_{\mathrm{g},}$ where the average particle size (diameter) can be given as a function of time as follows:

$$\bar{d} = d_0 \sqrt[3]{\frac{1}{\dfrac{k_\mathrm{n}}{2k_\mathrm{n} - k_\mathrm{g}} + \dfrac{{k_\mathrm{g}}^2 - k_\mathrm{n}k_\mathrm{g}}{\left(k_\mathrm{g} - 2k_\mathrm{n}\right)\left(2k_\mathrm{n}e^{\tau} + k_\mathrm{g} - 2k_\mathrm{n}\right)} + \dfrac{k_\mathrm{g}k_\mathrm{n}}{\left(k_\mathrm{g} - 2k_\mathrm{n}\right)^2}\left[k_\mathrm{g}[\mathrm{A}_1]_0 t - \ln\dfrac{2k_\mathrm{n}e^{k_\mathrm{g}[\mathrm{A}_1]_0 t} + k_\mathrm{g} - 2k_\mathrm{n}}{k_\mathrm{g}}\right]}}$$

Other possibilities of deriving exact and useful approximate formulas will be discussed on the poster.

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Synthesis and characterization of silica-coated magnetite nanoparticles modified with bis (pyrazolyl) triazine ruthenium (II) complex and the application of these nanoparticles as a highly efficient catalyst for the hydrogen transfer reduction of ketones

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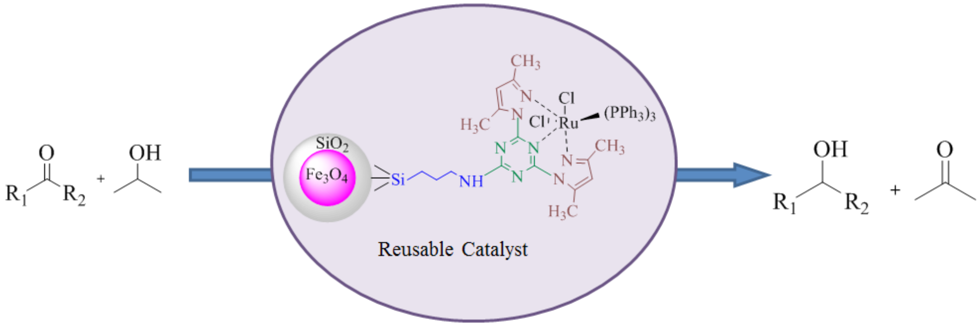
Keywords: magnetic nanoparticles, ruthenium complex, reduction, hydrogen transfer reactions

A facile and efficient method was represented for modifying the surface of silica-coated Fe_3O_4 magnetic nanoparticles with bis (pyrazolyl) triazine ruthenium (II) complex **(**MNPs@BPT-Ru(II)**)**. Field emission scanning electron microscopy (Fe-SEM), TGA/DTA analysis (TGA/DTA), X-ray powder diffraction (XRD), FTIR spectroscopy, Vibrating sample magnetometer (VSM) and Energy dispersive X-ray spectrometry (EDS) techniques were employed for characterizing the structure of these nanoparticles. MNPs@BPT-Ru(II) nanoparticles proved to be a magnetic, reusable and heterogeneous catalyst for the hydrogen transfer reduction of ketone derivatives. Also, highly pure products with excellent yields were obtained in the presence of this catalyst in relatively short times. The comparison of this catalyst with those previously used for the hydrogen transfer reactions proved the uniqueness of MNPs@BPT-Ru(II) nanoparticle which is due to its inherent magnetic properties and its large surface area. The represented method also had the other advantages like simple conditions, environmentally friendliness, high recovery ability, easy work-up and low cost.



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Preparation, characterization and catalytic activity of Cu-Sn bimetallic nanopowder synthesised *via* mechanical milling

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Keywords: bimetallic nanopowder, milling, XRD-SEM-DLS, catalytic activity

The controlled synthesis of bimetallic nanomaterials have recently attracted considerable attention. Numerous bimetallic structures show a variety of functionalities as well as performance in catalytic activity, selectivity, and stability, often superior to monometallic nanomaterials. This stems from the synergetic effects between the two metals. As a result of this cooperation, bimetallic catalytic systems are capable of achieving chemical transformations, which are not possible when monometallic catalysts are employed. This synergy is due to the fact that different components of the catalyst have specific function in the overall reaction mechanism and the various functions may complement each other. Several methods are available for the synthesis of metallic nanopowders. They include atomization, electrolysis, pyrolysis, chemical reduction methods, ball milling (mechanical milling), etc. Mechanical milling was demonstrated as a very efficient technique in the fabrication of bimetallic powders.

During this work, a mixture of copper and tin powders was milled in the presence of various solid and liquid organic additives (*e.g.,* oleylamine, ethylene glycol, dimethyl carbonate, polyethylene glycol, polyvinylpyrrolidon, cetyl trimethylammonium bromide). The effect of additives was investigated by X-ray diffractometry, scanning electron microscopy, and dynamic light scattering measurements. The catalytic activities of the various samples were tested in the reduction of aryl and heteroaryl nitro compounds.

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Monodispersed Ni and Ni-Co nanoparticles capsulated with silica shell for an enhanced stability of dry reforming of methane

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Keywords: monodispersed Ni and Ni-Co nanoparticles, silica encapsulation, nanoreactor, stability, dry reforming of methane

Transition metals such as Ni-based reforming catalysts are more favorably applied compared to precious metal-based ones for dry reforming of methane (DRM) due to its lower price. Even though Ni-based catalysts possess a comparable activity for DRM reaction, industrial applications of those Ni-based catalysts are limited due to their thermal instability by an easy sintering of the supported Ni particles to form less active larger aggregates at a high temperature as well as significant coke formation on the surfaces of the agglomerated Ni nanoparticles [**1**]. Therefore, the synergetic effects of the oxophilic Co nanoparticles can be boosted by preparing Ni-Co bimetallic catalysts not only for an enhanced activity of reforming reactions but also sustained stability of the catalysts by suppressing the aggregations of Ni nanoparticles as well as coke formations [**2**]. However, due to an inherent limitation of the heterogeneity of the supported active metals such as heterogeneous metal distributions and agglomerate formation at a high temperature reaction, the intrinsic roles of monodispersed Ni or bimetallic Ni-Co nanoparticles are still unrevealed clearly in terms of those characteristics. In the present study, the model nanoreactor composed of the SiO_2-encapsulated Ni nanoparticles (Ni@SiO_2) and bimetallic ones (Ni-Co@SiO_2), which is capable to retain the pristine particle sizes even under high temperature reaction, was successfully synthesized by following the well-known typical nanoparticle preparation methods. The Ni@SiO_2 and Ni-Co@SiO_2 catalysts were prepared by a thermal decomposition of metal precursors in the hot oleylamine solvent. The SiO_2–coated metal nanoparticles were synthesized on the dispersed nanoparticles in cyclohexane by microemulsion method. The dried Ni@SiO_2 and Co-Ni@ SiO_2 catalysts were in-situ reduced in a flow of 5% H_2/N_2 while the reactor was heated up to the reaction temperature of 700 ^{o}C. After the stabilization of the temperature, the reactant gas composed of $CH_4/CO_2/N_2$ at a ratio of 1/1/2 was fed to reactor at a space velocity of 18000 L/ kg_{cat} h^{-1}. The representative HRTEM images of the encapsulated Ni@SiO_2 revealed the well-synthesized structures with a high thermal stability with insignificant aggregations as shown in **Figure 1**, and the catalytic activity of DRM was stably kept for more than 100 h on stream without any significant activity loss, which were further confirmed by XPS, ICP-AES, and STEM-EDS mapping analysis.

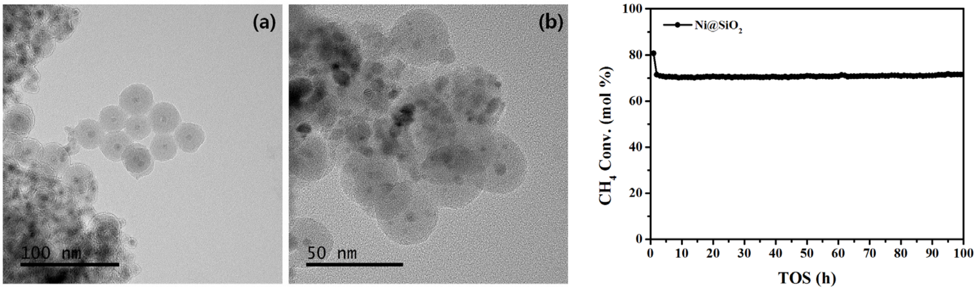

Figure 1. HRTEM images (left) of (a) fresh and (b) used Ni@SiO$_2$; and catalytic activity (right)

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T7: Combustion kinetics and catalysis

Poster

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Kinetics of hydrogen abstraction reactions from polycyclic aromatic hydrocarbons by OH radical

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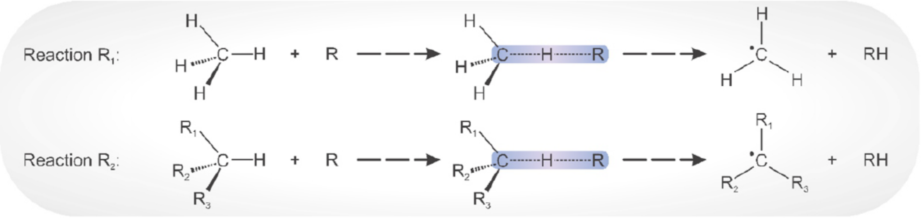
Keywords: kinetics, hydrogen abstraction, Polycyclic Aromatic Hydrocarbons, hydroxyl radical, RC-TST

This work applies the Reaction-Class Transition State Theory (RC-TST) method for evaluation of the thermal rate constants of hydrogen abstraction reaction by OH radical from Polycyclic Aromatic Hydrocarbons (PAHs), in the temperature range of 300-3000K. The reaction between hydroxyl radical and PAHs is of great importance, since OH is one of the main oxidizing agents of unsaturated hydrocarbons in the troposphere [1], as well as one of the main initiating species in PAHs combustion [2].

The RC-TST method used in this study, proved to be a cost-effective and accurate method for estimating reaction rate constants [3]. It takes advantage of the common structure denominator of all reactions in a given family to obtain rate expression of any reaction within a reaction class. The most important reaction in RC-TST framework is the reference reaction, since it is used to extrapolate all other reaction rate constants.

Parameters for the RC-TST were derived from theoretical calculations at M062X/ccpVTZ level of theory, using a set of 34 representative reactions. The energetic parameters for reference reaction have been calculated at several higher-level methods such as CBS-APNO and G3B3. Reference reaction rate constant has been calculated using the Canonical Variational Transition State Theory with the Small Curvature Tunneling approximation (CVT/SCT) as applied in PolyRate package. To take into account the tunneling effect in the training set, the Eckart's method was employed. The explicit treatment of hindered rotors was carried for low-frequency internal rotations. The results show, that RC-TST method can predict the thermal rate constants within reaction class with a very good accuracy.

Figures



$$
\begin{array}{ccccccccccccc}
k^{TST}(T) = & \boxed{\sigma} & \cdot & \kappa(T) & \cdot & c_{HR} & \cdot & \frac{k_B T}{h} & \cdot & \frac{Q^{\ddagger}(T)}{\Phi^{R}(T)} & \cdot & \exp\left(\frac{-\Delta V^{\ddagger}}{k_B T}\right) & \\
k^{RC-TST}(T) = & f_{\sigma} & \cdot & f_{\kappa} & \cdot & f_{HR} & \cdot & & \cdot & f_{Q} & \cdot & f_{V} & \cdot\, k_{R1}(T)
\end{array}
$$

Figure 1. The scheme of RC-TST method application. Reaction R_1 is the reference reaction and R_2 is an arbitrary reaction with the same reactive moiety but different substituents. Thermal rate constant for any reaction within given class in RC-TST is a product of reference reaction rate constant $k_{R1}(T)$ and the symmetry (f_{σ}) , tunneling (f_{κ}), partition function (f_Q), potential energy (f_V), and hindered rotations (f_{HR}) factors.

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Scientific and engineering issues of the CO oxidation on nanocomposite MnCeO$_x$ catalysts

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Keywords: oxide nanocatalysts, CO oxidation, mechanism and kinetic modeling, active sites and reaction intermediates

Since many decades, the oxidative conversion of carbon monoxide is one of the most common "model" reactions in Catalysis, with also great environmental and technological concerns due to high toxicity of CO, also boosting the formation of ozone in metropolitan areas, and the fact that CO behaves as a poison in some important catalytic technologies (e.g., Ammonia, Fuel Cells, etc.). Although supported noble metals currently dominate the catalyst market for environmental applications, including total and preferential CO oxidation in hydrogen streams (PROX), an incessant research interest is devoted to transition metal oxide (TMO) systems, for obvious economic reasons and a performance at low-medium temperature (<573K), actually comparing to metal catalysts [1]. In fact, metals and TMO's feature a CO oxidation pattern depending on different interactions with substrate and oxygen, even though catalyst chemistry and reaction environment (i.e., temperature, reagent pressure and molar ratio) control mechanism and activity [1]. Therefore, this work is aimed at providing a thorough overview of the CO oxidation pattern of a nanocomposite MnCeO$_x$ catalyst (M5C1; Mn$_{at}$/Ce$_{at}$, 5) in wide ranges of temperature (293-533K), CO-O$_2$ pressure (0.00625-0.025 atm), CO/O$_2$ molar ratio (0.25-4.0), CO$_2$ co-feeding (0.0-0.10 atm) and conversion level (0-100%) [2]. Systematic activity data under kinetic regime and mechanistic evidences signal the occurrence of competitive adsorption phenomena, although the abstraction of O-atoms from the Mn^{IV} active sites is rate-determining (*r.d.s.*). A concerted redox mechanism, L-H type, of five elementary steps leads to formal rate equations explaining empiric kinetics and fully predicting the reactivity pattern of the studied catalyst in the range of 293-533K (Fig. 1).

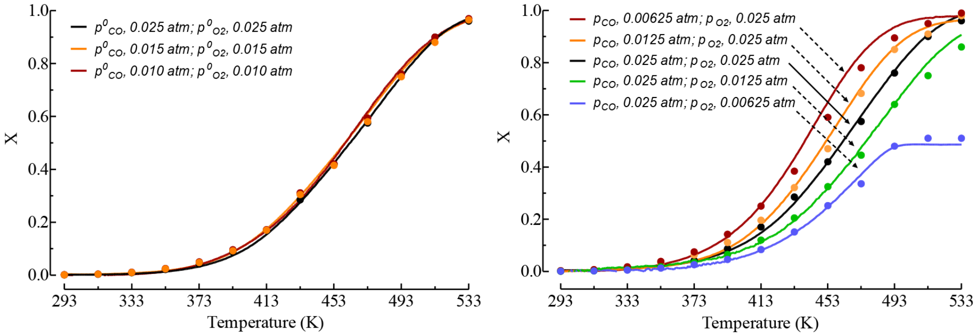

Figure 1. Predicted (symbols) and experimental CO conversion data (lines) in the range of 293-533K at different reagents concentration (left) and p_{0CO}/p_{0O2} ratio (right).

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In situ XAS and XRD study of CuFeAl-composite catalysts of CO oxidation

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Keywords: heterogeneous catalysis, CuO, CO oxidation, reduction

Catalytic oxidation of gasification products of solid fuels allows utilizing low-grade fuels such as lignite, peat, and firewood as well as various industrial wastes. At the same time catalytic combustion produces a significantly lower amount of harmful emissions then "traditional combustion" of fuels. CuFeAl-composite catalysts demonstrate high activity and stability in catalytic oxidation of gasification products of solid fuels. Moreover, the catalysts are inexpensive and ecologically clean. In this contribution we present our first results of *in situ* investigations of the catalyst state under reaction conditions. Since carbon monoxide is the main product of gasification of solid fuels we performed investigation CuO, Fe_2O_3, and CuFeAl-composite catalysts in CO and $CO+O_2$ mixture in a wide temperature range. We applied three methods: XANES, EXAFS, and XRD. XANES is very useful for identification of different chemical states of copper and iron and allows us to study the chemistry of the catalysts under reaction conditions. X-ray diffraction techniques allow us to study the phase composition, but, unfortunately, the technique cannot identify nanoparticles and amorphous phases. This shortcoming can be eliminated by EXAFS which may clarify the structure of local environment of copper and iron atoms even when their concentration is extremely low.

In situ XAS experiments were performed at the Structural Materials Science station at Kurchatov Center for Synchrotron Radiation. The spectrometer is equipped with high temperature chamber that allows collecting XAS spectra within temperature range from RT to 600°C in the gas mixture at atmospheric pressure. *Operando* XRD/MS experiments were carried out at the "High Precision Diffractometry II" station at "Siberian Synchrotron and Terahertz Radiation Center" and at a lab Bruker D8 Advance diffractometer (Boreskov Institute of Catalysis). The both diffractometers are equipped with XRK 900 reaction chambers (Anton Paar GmbH) that allow observing the diffraction patterns within temperature range from RT to 900°C in the reactant mixture at atmospheric pressure.

We found that fresh CuFeAl-composite catalysts consist of CuO, Fe_2O_3, and Al_2O_3. In a CO flow, the reduction of copper from Cu^{2+} to Cu^{1+} and Cu^0 started at temperature about 200°C; at 600°C copper is mainly in the metallic state. At the same time the reduction of iron started at temperature about 400°C and at 600°C about 20% of iron is in the metallic state. *Operando* XRD study allows us to determine the phase transition of iron-containing phase during the reduction in a CO flow. The reduction process occurs in the next manner: $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO$ and Fe^0. In $CO:O_2 = 2:1$ mixture, the reduction of copper from Cu^{2+} to Cu1+

started at temperature about 400°C and at 600°C about 50% of copper is in the Cu^{1+} state, whereas iron is slightly reduced to Fe^{2+} state at 600°C. The following increase the partial pressure of O_2 leads to shift initial reduction temperature to high temperature range.

Thus, the use of complimentary methods (XANES, EXAFS, and XRD) allows us to determine the chemical state of copper and iron, phase composition in the catalyst during the oxidation of CO. The data presented can facilitate to clarify the mechanism of oxidation of CO.

Acknowledgments

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Kinetics of *p*-xylene photocatalytic degradation on UiO66-NH_2 thin film under UV-LED irradiation

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Keywords: kinetics, *p*-xylene, photocatalytic degradation, UiO66-NH_2, thin film

In this research UiO66-NH_2 thin film was prepared by a solvothermal combined with dip-coating technique. The physico-chemical properties of obtained MOF were investigated by the methods of BET adsorption, XRD, SEM, FT-IR, TGA, UV-Vis and Raman spectroscopies. The kinetics of photocatalytic degradation of *p*-xylene under combined illumination of ultraviolet and visible irradiation over obtained UiO66-NH_2 thin film were carried out in a gradientless flow circulating system at room temperature and atmospheric pressure. The obtained results showed that UiO66-NH_2 thin film with the thickness of 4.2 μm, the specific surface area of 576 m^2/g, and a band gap energy of 2.83 eV formed in ball particles of 100−200 nm was synthesized. In this case the kinetics of the reaction was found to be written by fractional equations, describing the dependence of the reaction rate on the concentration of p-xylene, oxygen molecules, dissociative adsorbed water vapor, the photon flux, and inhibited by adsorbed CO_2 product. It imply that the reaction occurred at high surface coverages, molecular p-xylene and oxygen participated in the reaction in the form of surface molecular; water − in the forms of •OH and H^+. The reaction was proposed to follow the Langmuir-Hinshelwood mechanism.

Acknowledgment

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Characterization of various Pd loading on Co/SBA-15 prepared by co-impregnation for ethanol oxidation

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PdO/Co_3O_4 on SBA-15 with varied Pd loadings (0.2, 0.5 and 1 wt%.) is prepared by co-incipient wetness impregnation of the mixed precursors between $PdCl_2$ and $Co(NO_3)_2 \cdot {}_6H_2O$. Their physicochemical properties are studied by characterization with various techniques. Results from XRD, DR-UV–Vis, i-TPR and XAS, including X-ray XANES and EXAFS suggest that the cobalt species in the prepared catalysts is Co_3O_4 with spinel structure. The crystal size of Co_3O_4 preserves nearly the same size after the increase amount of Pd loadings indicating that the repulsions effect between those precursors and the SBA-15 are minimized. In addition, the structure of SBA-15 is not collapsed after calcination in air according to the present of characteristic peak in lower angle. Moreover, N2 adsorption–desorption analysis confirm that the PdO and Co_3O_4 on SBA-15 mostly locate inside the pore of the SBA-15 due to the decrease of hysteresis loop compared to the bare SBA-15. XPS, XANES and i-TPR analysis confirm that the Pd species is PdO. Interestingly, the ratio of Co_3+/Co_2+ in Co_3O_4 surface increases with the amount of Pd loading suggested by XPS. Zhu et al., 2013 reported that the richer of Co_3+ species in Co_3O_4 storing abundant of surface lattice O_2- played an important role for oxidation of toluene and propane giving faster reaction rate. Thus, the catalysts will be tested in oxidation reaction and optimum reaction condition will be determined.

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Zr, Co, Ti, La, CePd-MeO$_x$/Al$_2$O$_3$ (Me=) catalysts for methane combustion

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Keywords: CH$_4$ combustion, Co, Zr, Ti, La, Ce modified palladium catalysts, sulphur poisoning

Methane, being a greenhouse gas, plays a significant role in the global warming. Most of the catalysts, designed for methane combustion, are based on palladium – separately or in combination with different metals or metal oxides, supported on alumina. The main problem in the practice is the deactivation and the needed thermal stabilization of the support and the catalytic active phase could be found in the introduction of rare earth oxides into the existing catalytic systems. The preparation of a highly active and stable Pd+Co/γ-Al$_2$O$_3$ catalyst has been reported in our work. The effect has been explained by the stabilization of palladium as PdO on the support due to strong interaction between Pd particles and the surface cobalt oxide phase. La$_2$O$_3$ is an excellent stabilizer of the specific surface area of supports like Al$_2$O$_3$ and ZrO$_2$. CeO$_2$ is also well known as an alternative for stabilization of PdO since it hinders the PdO reduction and promotes Pd re-oxidation when PdO–CeOx contact is available. In searching for thermally stable catalysts for methane combustion, the single-component (Pd/Al$_2$O$_3$, CoO$_x$/Al$_2$O$_3$,) and multi-component (Pd+CoO$_x$/Al$_2$O$_3$, Pd+CoO$_x$/La$_2$O$_3$-Al$_2$O$_3$, Pd/La$_2$O$_3$-CeO$_2$-Al$_2$O$_3$ and Pd+CoO$_x$/La$_2$O$_3$-CeO$_2$-Al$_2$O$_3$) samples were prepared. The catalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR), transmission electron microscopy (TEM), Infrared spectroscopy (IRS) and reaction kinetics measurements. Finely dispersed palladium particles were formed on the surface of all samples. Pd^{2+} and Pd^{4+} are both present on the surface of the fresh catalysts modified with Co only, while the major part of the surface palladium in the La and Ce containing samples is in the form of Pd^0. The following order of activity is observed: Pd+CoO$_x$/Al$_2$O$_3$>Pd+CoO$_x$/La$_2$O$_3$-CeO$_2$-Al$_2$O$_3$>Pd+CoO$_x$/La$_2$O$_3$-Al$_2$O$_3$>Pd/Al$_2$O$_3$, i.e. the modification of Pd/Al$_2$O$_3$ with Co significantly improves its catalytical activity. It is very likely that, when La and Ce are deposited before the Co deposition, the formation of cobalt surface phase is hindered as well as the further stabilization of PdO phase. The Pd+CoO$_x$/Al$_2$O$_3$ sample demonstrates remarkable stability after ageing.

For the hydrothermal stability improvement, the catalytic system might be doped with zirconia, while for the resistance towards sulphur poisoning the catalyst should contains oxides that form unstable S-containing surface compounds (sulphites instead of the thermally stable sulphates) and the modification of the catalyst with titania could offers such probability. In order to explore the possible enhancement of the La$_2$O$_3$-CeO$_2$-Al$_2$O$_3$ – system, the following catalysts were synthesized: Pd/ZrO$_2$-La$_2$O$_3$-CeO$_2$-Al$_2$O$_3$ and Pd/TiO$_2$-La$_2$O$_3$-CeO$_2$-Al$_2$O$_3$ via sol-gel technique. The stability tests were performed at 455 ^{o}C and water vapour content of 2.2 vol. %, while the sulfur resistance was investigated by treatment at SO$_2$ concentration of

55 ppm for 18 h. The obtained data revealed out that after the work in presence of SO_2 both samples lost significant extent of their activities (92 % for Pd/ZrO_2-La_2O_3-CeO_2- Al_2O_3 and 88 % for Pd/TiO_2-La_2O_3-CeO_2- Al_2O_3), however after operation at 495 ^{o}C for 8 hours the zirconia – based sample restored just 3 % of its initial activity, while the based on titania has returned to its 25 % activity of the fresh sample. Therefore, one may consider the doping of the Pd-based catalytic systems with TiO_2 as perspective approach for development of sulfur – tolerant catalyst for methane combustion.

Acknowledgments

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Catalytic methane reforming into synthesis-gas over developed composite materials prepared by combustion synthesis

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Keywords: SHS, combustion synthesis, catalysts, dry reforming, partial oxidation, methane

Works on research of intermetallic compounds of transition metals as a contact mass for the conversion of methane were carried out. The method of self-propagating high temperature synthesis (SHS) was used for the synthesis of catalysts. Catalysts of this type are characterized by thermal stability, mechanical strength and high thermal conductivity. SHS is a heterogeneous combustion process, which proceeds without the participation of oxygen with low energy consumption, high efficiency and rapidity. The very high temperature develops in the reaction zone. The catalysts of oxidative and carbon dioxide reforming of methane were prepared by SHS method from powder mixtures of metal oxides. Self-propagating combustion wave was initiated after pressing the batch and preheating to 400-600°C. The temperature of the combustion front has evolved to 830-1150°C. Experiments on the catalytic reforming were carried out on flow type installation at atmospheric pressure in a tubular quartz reactor with a fixed catalyst bed.

Mixtures of the ($Ni(NO_3)_2$ - $Co(NO_3)_2$ - $Al(NO_3)_3$ - $Mg(NO_3)_2$) salts are used for the synthesis of catalysts. The reactions resulting in the formation of $NiCo_2O_4$, Co_2AlO_4 and $CoAl_2O_4$ spinels and AlCo, $AlNi_3$ intermetallic compounds occur at preparation of samples by solution combustion synthesis. Magnesium ions are almost completely replaced by cobalt ions in the $MgAl_2O_4$ spinel. As a result, the $CoAl_2O_4$ and Co_2AlO_4 spinels are formed in the reaction products. Investigation of the activity of catalysts based on the initial mixture of $Ni(NO_3)_2$ - $Co(NO_3)_2$ - $Al(NO_3)_3$ - $Mg(NO_3)_2$ produced in the solution combustion synthesis process was carried out in the reaction of dry reforming of methane. 100% methane conversion at 750°C was carried out on the catalyst with 47% $Ni(NO_3)_2$, whereas the conversion of CO_2 reached 81.7% at a temperature of about 900°C. Hydrogen yield reached 99.2%, yield of CO - 99.1% in the ratio of $H_2/CO = 1.2$. The activity corresponded to 0.96 mol H_2/g Cat × h and 0.78 mol CO/g Cat × h. The catalyst of similar composition is active and selective for the partial oxidation of methane to synthesis gas. The highest results were obtained on reduced catalyst samples. Thus, effective catalysts for the production of synthesis gas from methane of natural gas as a result of studies have been developed. The modern method of self-propagating high temperature synthesis and solution combustion method were used for the synthesis of catalysts. XRD and scanning electron microscopy of samples with chemical analysis before and after catalysis indicated on single-phase of produced systems and the absence of significant changes in the phase composition after experiments. The activity of catalysts obtained in the solution combustion process was examined in carbon dioxide reforming of methane and partial oxidation of methane to synthesis gas.

Acknowledgments

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T8: Chemical kinetics in solution, gas or solid phases

Oral

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Kinetics of nickel-oxalate precipitation in a well-stirred batch system

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Keywords: spectrophotometry, induction period, heterogeneous kinetics

Producing self-assembled inorganic precipitate micro and macro structures with tailored properties may pave the way for new possibilities in e.g., materials science and pharmaceutical industry. One set of important parameters to maintain appropriate control on the yield falls in the frame of reaction kinetics which affects the possible coupling between hydrodynamics and chemical reactions under flow conditions. In this study we present a spectrophotometric method to experimentally determine the characteristic time scale for sufficiently slow precipitation reactions. It is also shown that the nickel-oxalate model system - despite of the fast chemical complexation equilibria taking place - can be kinetically described by either the Classical Nucleation Theory or the classical homogeneous kinetics approach. Our results suggest that easy-to-handle power law functions may be applied to precipitation systems if the characteristic time is carefully chosen thus the role of the solid phase is negligible and the reaction mechanism is simple.

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Kinetic modelling and thermodynamic analysis for hydrodeoxygenation of isoeugenol over bifunctional Pt-H-beta zeolites

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Keywords: hydrodeoxygenation, kinetics, modelling, phoenolic compounds

Hydrodeoxygenation (HDO) of lignin based model compounds, such as isoeugenol (Fig. 1a), is currently under intensive research efforts. In this work hydrodeoxygenation of isoeugenol is successfully demonstrated over bifunctional Pt-H-beta-catalysts with varying Si/Al ratio producing propylcyclohexane as the main product with high activity and selectivity. Typically HDO experiments were performed at 200°C under 30 bar total pressure in hydrogen in an autoclave using dodecane as a solvent. The catalysts were prepared by evaporation impregnation method using hexachloroplatinic acid as a Pt precursor. The catalysts were characterized with several physico-chemical methods (pyridine adsorption desorption FTIR, TEM, CO chemisorption, nitrogen adsorption, thermogravimetrical analysis). The kinetic experiments were performed using small catalyst particle sizes (< 63 μm) in order to avoid mass transfer limitations. The samples were withdrawn at different times and analyzed in GC. The unknown products were confirmed by GC-MS. In addition to kinetics analysis, also modelling of kinetics and thermodynamic analysis using the Gibbs-Helmholtz equation were performed. The results showed that the main reaction route goes from a rapid hydrogenation of isoeugenol to dihydroeugenol followed by deoxygenation of the latter forming propylbenzene as an intermediate and subsequently propylcyclohexane as the main product. The highest selectivity to propylcyclohexane (89%) was obtained in 4 h at 200°C under 30 bar total pressure at complete conversion over Pt-H-beta-300 exhibiting the Si/Al ratio of 300 and the lowest acidity. When increasing the amount of Brønsted acid sites in the catalyst, lower selectivity towards the main product was achieved. Special emphasis was put on the sum of the masses of reactant and products present in the liquid phase and determined by GC. Typically this sum decreased with increasing catalyst acidity being 63% with the mildest catalyst. The reason for this result is formation of dimers and oligomers confirmed by GC-MS and thermogravimetric analysis of the spent catalysts. The kinetic model was proposed (Fig. 1b) and thermodynamic analysis of isoeugenol HDO was made taking into account stoichiometry of different reactions in the liquid phase. The results revealed that hydrogenation became unfeasible at higher temperatures. Detailed reaction mechanism and kinetic analysis will be discussed in the final work and the catalyst properties will be correlated with their performance.

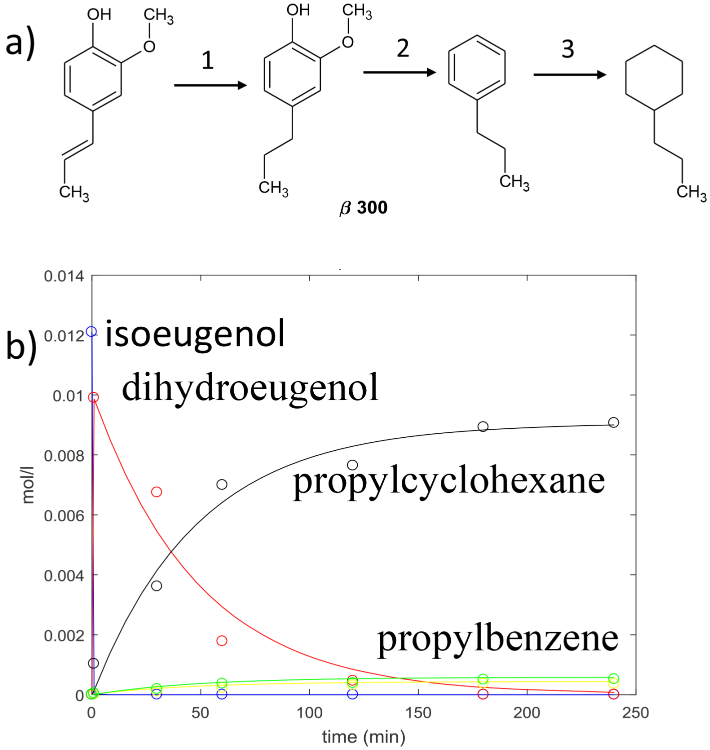

Fig. 1. a) Reaction scheme and b) HDO of isoeugenol over Pt-H-Beta-300 catalyst at 200°C under 30 bar.

Poster

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Autocatalytic oxidation of tritionate ion by iodate in a strongly acidic medium

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Keywords: tritionate ion, autocatalysis-driven clock reaction, kinetics

The trithionate–iodate reaction has been studied spectrophotometrically in an acidic medium at 25 C in phosphoric acid/dihydrogen phosphate buffer, monitoring the absorbance at 468 nm at the isosbestic point of the iodine–triiodine system and at I= 0.5 M ionic strength adjusted by sodium perchlorate. The main characteristics of the title system are very reminiscent of those found recently in the pentathionate–iodate and the pentathionate–periodate reactions, the systems paving the way for classifying clock reactions. Thorough analysis revealed that the direct trithionate–iodate reaction plays a subtle role only to produce a trace amount of iodine ion via a finite sequence of reactions:

$$3\mathrm{S_3O_6^{2-}} + 4\mathrm{IO_3^-} + 6\mathrm{H_2O} \rightarrow 9\mathrm{SO_4^{2-}} + 4\mathrm{I^-} + 12\mathrm{H^+}.$$

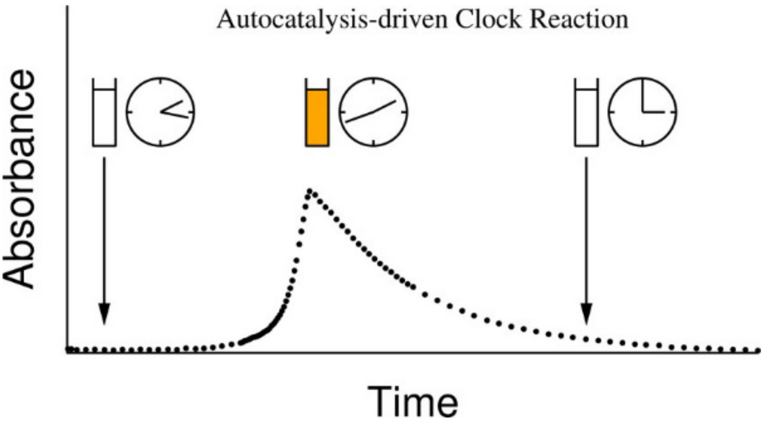
Once the concentration of the iodine ion reaches a certain level, then the reaction is almost exclusively governed by the trithionate—iodine and the iodide—iodate reactions:

$$\mathrm{S_3O_6^{2-}} + 4\mathrm{I_2} + 6\mathrm{H_2O} \rightarrow 3\mathrm{SO_4^{2-}} + 8\mathrm{I^-} + 12\mathrm{H^+}$$

$$\mathrm{IO_3^-} + \mathrm{I^-} + 6\mathrm{H^+} \rightarrow 3\mathrm{I_2} + 3\mathrm{H_2O}.$$

This simple three-step Landolt-type kinetic model is proposed to describe adequately the most important kinetic features of the title system that can easily be extended to a feasible sequence of elementary and quasi-elementary reactions.

Figure



A typical experimental curve of the title reaction at 468 nm.

Acknowledgments

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Kinetics of ligand substitution in iminodiacetate complexes of Ni(II) and Co(II) in aqueous solutions

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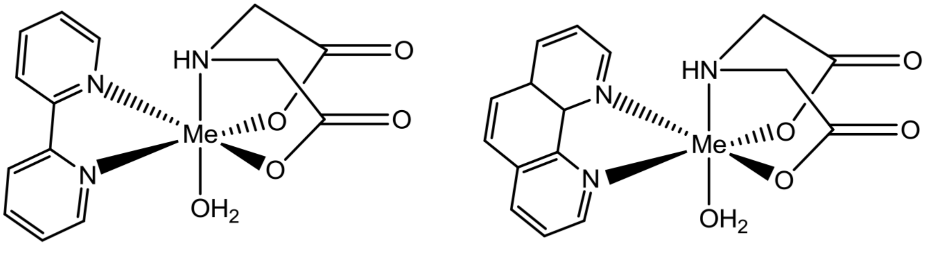
Keywords: iminodiacetate anion, substitution reaction, nickel(II) and cobalt(II) complexes, stopped-flow method

In the literature, it is described that policarboxylate coordination compounds of transition metal ions can be considered as new, potentially attractive superoxide dismutase (SOD) mimetics [1]. The role of such compounds is to scavenge of superoxide free radicals ($O_2{\cdot}^-$). Furthermore, some of the ternary complexes of the functionalized dicarboxylates like iminodiacetate, pyridine-2-6-dicarboxylate and oxydiacetate as primary ligands and N-based chelator (α-diimine) as auxiliary ligands e.g. 1,10-phenanthroline (phen) or 2,2'-bipyridine (bipy), were found to exhibit remarkable antimicrobial and catalase properties [2].

We report the results of the kinetic measurements of ligand substitution in the iminodiacetate complexes of Co^{2+} and Ni^{2+}. The rate of the substitution reaction of two aqua ligands in the coordination sphere of binary metal(II)-ida complexes by the auxiliary ligand resulting in ternary complex formation is investigated by using a spectrophotometric (UV-Vis) *stopped-flow* technique. The investigations show the impact of the type of the auxiliary ligands (phen and bipy) as well as the impact of the coordination center (metal ions) on the rate of substitution reaction of Co(II) and Ni(II) complexes have been discussed. The mechanisms of studied reactions were proposed.



Me = Co^{2+} or Ni^{2+}

Figure 1. The studied iminodiacetate complexes of cobalt(II) and nickel(II).

Acknowledgments

This work was supported by National Science Centre, Poland, under Grant number 2015/19/N/ST5/00276.

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Crazy-clock behavior in the periodate-arsenous acid reaction

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Keywords: crazy-clock behaviour, Landolt reaction

Stochastic kinetics has a very extent mathematical description with various potential applications. In case of nonlinear redox reactions, three systems were proven to exhibit irreproducible individual kinetic curves.

It is clearly demonstrated that the arsenous acid–periodate reaction displays crazy-clock behavior when statistically meaningful number of kinetic runs are performed under "exactly the same" condition. Both extensive experimental and numerical simulation results gave a convincing evidence that the stochastic feature of the title reaction is rather originated from the imperfection of mixing process and neither local random fluctuations nor initial inhomogeneity alone is capable of explaining adequately the observed phenomena. Imperfect mixing is manifested – in practice – in the unintentional and inherent formation of dead volumes where concentration of the reactants may even significantly differ from the ones to be measured in case of a completely uniform concentration distribution and the system may spend enough time there under imperfectly mixed conditions to complete the nonlinear chemical process. Furthermore, it is also shown that a more efficient mixing, i.e. smaller dead volume size and shorter residence time being spent in the dead volume, does not necessarily mean Landolt times smaller than the one to be measured at a completely homogeneous condition. Evidently, "initial" concentration of the reagents in the dead volume − and of course in rest of the solution − greatly influences the Landolt time to be measured in case of an individual kinetic run and may therefore show either positive or negative deviation from the Landolt time belonging to the completely homogeneous state. As a result, less efficient mixing may either accelerate or decelerate the rate of a nonlinear autocatalytic reaction at a macroscopic volume level.

Perhaps the most surprising result is that the arsenous acid–periodate reaction in itself is capable of featuring stochastic behavior even if the arsenous acid–iodate reaction is completely uncoupled by an increase of pH. The result is striking in a sense that in case of all the known systems so far the highly autocatalytic nature of the given reactions is experimentally justified. In this case however, the measured absorbance-time curves do not display directly the characteristic sigmoidal-shaped kinetic curve. Since detailed and reliable kinetic model for the arsenous acid–periodate reaction has not yet been published in the literature, further experiments are being progressed in our laboratory to unravel the secret of this fascinating system.

Acknowledgments
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Reactions following electric explosion of iron and alloy wires in liquid media

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Keywords: plasma, vaporization, decomposition of liquid, iron alloy, explosion of wire

Electric explosion of wires (EEW) is a method for preparation of metallic nanoparticles. An intense short current pulse in a thin wire results in a „micro-explosion”, i.e. the wire melts, evaporates, and even plasma is formed around it for a short while [1], providing space for a great variety of reactions. The products condense immediately after the collapse of the plasma. Typical technical parameters can be e.g. 0.2 mm wire diameter, 10^{10} A m^2 current density for ca. 10 – 12 μsec. The main end-product usually is composed from spherical metallic globuli in various sizes with a cover layer formed on them from products of direct interaction with the cooling media („coarse fraction”). The other sort of end-products („fine fraction”) is composed from the vaporized and condensed products of reactions taking mainly place in the short life-time plasma bubble. From the analysis of end-products various former stages of reaction paths can be traced.

Several metal /liquid combinations were studied in our EEW experiments, namely iron in water, ko33 FeCrNi alloy in water, iron in paraffin oil, Kovar (FeCoNi) alloy in ethylene glycol and in siloxane.

Primary emphasis was laid on analysis of components of fine fraction with techniques of XRD, SEM, HRTEM and Mössbauer spectroscopy. From characterizations of products a generalized scheme could be constructed (Fig. 1). In cases of each studied metal/liquid pairs the relative weight of processes are different as can be deduced form the analyses of given products.

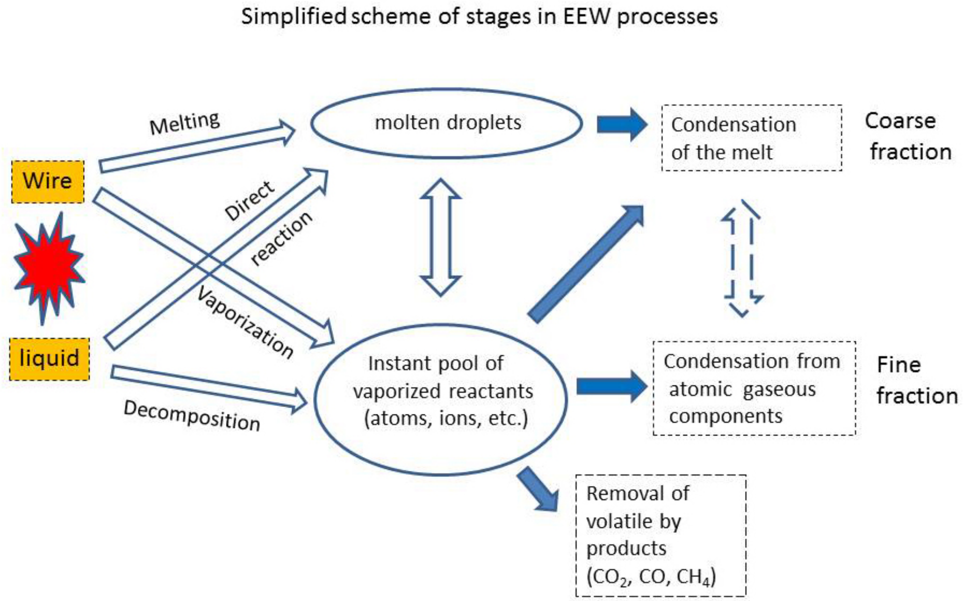

Figure 1. Simplified scheme of various stages during and following immediately EEW processes

Acknowledgements

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The kinetics of aquation of VO(IV) iminodiacetate complex with 2,2’-bipyridine induced by Fe(III) ions

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Keywords: aquation, vanadium(IV) complexes, kinetics, iminodiacetate complex

Aquation is one of a type of substitution reaction. During the aquation, the ligand is substituted by water molecules. The kinetics of substitution reactions of the [VO(ida)(H_2O)]·H_2O binary complex (where ida = iminodiacetic anion) with 2,2’-bipyridine (bipy) had previously investigated in aqueous solutions [1]. The kinetics of the aquation reaction of oxydiacetate complex has been known in the literature [2-3].

The kinetics of aquation of [VO(ida)(bipy)]·2H_2O complex (Fig.1), induced by Fe(III) ions, were examined. Kinetics measurements have been studied spectrophotometrically (UV-Vis). The progress of the aquation reaction of VO(ida)(bipy), promoted by Fe^{3+} ions, was monitored at 510 nm. This spectral wavelength is not sensitive to absorptions of [Fe(ida)(H_2O)$_3$]$^+$. The studies have been carried out at different temperatures with variable concentrations of Fe(III) ions.

The values of the observable reaction rate constants were calculated. Moreover, based on the Arrhenius and Eyring equations the activation parameters of the aquation reaction were calculated for the spontaneous step of reaction and the step of reaction induced by Fe^{3+} ions. Furthermore, the mechanism for the aquation of the VO(ida)(bipy) complex, induced by Fe(III) ions, has been proposed.

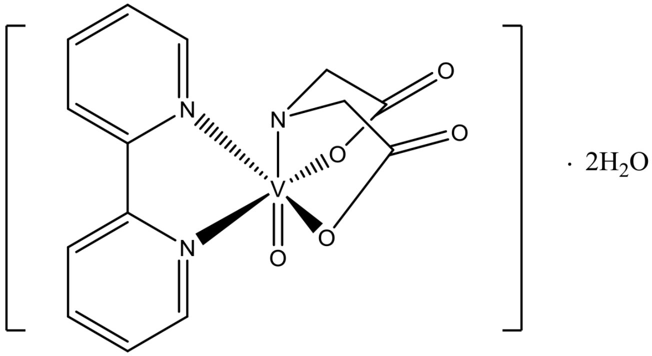

Figure 1. Structure of 2,2’-bipyridyl(iminodiacetato)oxidovanadium(IV) dihydrate

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This work was supported by National Science Centre, Poland, under Grant number 2015/19/N/ST5/00276.

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Effect of magnetic fields on the radical yield in mixed micelles {hydroperoxide-cationic surfactant}

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Keywords: micellar catalysis, magnetic field, hydroperoxide decay, free radicals, cationic surfactants

Hydroperoxides (LOOH) are the primary oxidation products of most organics including hydrocarbons and lipids. LOOH are amphiphilic compounds and have surface activity at interphase boundaries. By this reason, LOOH form mixed micelles with micelle-forming surfactants (S): mLOOH + nS ⇔ {mLOOH…nS}. Contrary to anionic and nonionic surfactant, cationic surfactants (S^+) were found to catalyze the hydroperoxide decomposition into free radicals in mixed micelles.

The interaction of magnetic fields (MFs) with living organisms is a rapidly growing field of investigation as well as an increasing interest in magnetic and spin effects caused by the increased use of magnets in various areas. Those chemical processes in which radicals, radical ions, and paramagnetic species are generated or involved make the main contribution to the magnetic effects. Unpaired electrons of such species are carriers of spin magnetism and interact with magnetic fields.

In this study, we estimated the magnetic effect on the radical yield in mixed micelles {nLOOH..S^+} with tertbutyl hydroperoxide and some S+: cetyltrimethyl ammonium bromide (CTAB), cetylpyridinium bromide (CPB) and acetylcholine chloride (ACh). An estimate was made for different values of the magnetic field strengths and for different concentrations of the cationic surfactant. The retarding effect of the magnetic field on the yield of radicals in the micellar system was observed and the field dependence was determined. At low S^+ concentration ($[S^+] <$ cmc) in the absence of mixed micelles in molecular solution, small acceleration of the radical formation was found. It is noteworthy that the retardation effect of the magnetic field in micellar system decreases in the presence of paramagnetic particles such as oxygen and relatively stable radicals.

Acknowledgments

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Propane oxidative dehydrogenation over binary mixtures of alkaline and alkaline earth chlorides supported on La-Y zeolite

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Keywords: oxidative dehydrogenation, propane, alkali chloride, alkaline earth chloride, zeolite

Currently, light olefins which are base chemical for petro chemistry, mainly produced by cracking of naphtha and crude oil while due to the depletion of fossil fuels, it is necessary to find other methods for production of light olefins. Despite of the great effort, the ODH process has not been implemented on large scale yet. Several catalytic systems attracted attention, like supported transition metal oxides or alkali chlorides. However, the former one suffers from the insufficient selectivity to olefins and overoxidation to the CO_2, the catalysts based on alkali chlorides suffer from low activity and relatively high reaction temperature necessary. Recently, some of us reported on high ethane conversion and selectivity to ethylene at relative low temperature (500°C) over molten mixtures of chlorides supported on zeolite[1]. In this study, the investigation of binary alkaline chloride $RbCl/MgCl_2$ mixture (with the eutectic composition) behavior, supported over lanthanum exchanged FAU zeolite, in the oxidative dehydrogenation of ethane to ethylene has been surveyed. The support was prepared by solid-state ion exchange of NH4-Y with $LaCl_3.7H_2O$ under nitrogen flow at 500 °C, and the catalyst was prepared by thermal treatment of mechanical mixture of the alkali and alkaline earth chlorides with La-FAU in the flow of helium at 500°C. Synthesized catalysts were tested in the oxidative dehydrogenation of propane in plug-flow fixed-bed tube-like reactor at atmospheric pressure. The reaction mixture consists of $C_3H_8/O_2/He = 3/15/82$ vol. % with a total flow of 50 cm^3 min^{-1} STP at 500 °C. Characterization of the precursor, fresh and spent catalysts obtained by powder XRD, SEM, N2 adsorption/desorption isotherms, and Raman spectroscopy to achieve information about crystallinity, morphology, textural properties and surface chemistry of the catalysts. Propylene was the main product of the reaction having selectivity higher than 90%. CO_2 selectivity was below 3% and other product traces, like methane and other hydrocarbons were detected. Conversions reached up to 90% resulting in yield of olefins reaching 80%. Catalysts exhibit some deactivation, when conversion of the propane is decreasing in time on stream, but high and almost constant selectivity toward individual products are preserved. It seems the molten over layers of alkaline chlorides provide a dynamically rearranging reaction interface, which minimize the re-adsorption of olefins and inhibit the undesired combustion reaction. More details such as effect of reaction temperature, contact time, proposed mechanism, will be presented at conference. Binary eutectic mixtures of alkaline and alkaline earth chlorides supported on zeolites represent effective catalytic systems for propane oxidative dehydrogenation to propylene. High activity exhibit these catalysts at significantly lower temperatures than is usually applied for alkali or alkaline based catalysts. It is main advantage of this system and deserves to be investigated in more details.

Acknowledgments

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Diffusion effects in liquid-phase epoxidation of alkenes by hydrogen peroxide using titanosilicates as catalysts

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Keywords: titanosilicate, alkenes, epoxidation, diffusion

Titanosilicates with MFI structure are widely used as catalysts for numerous oxidation reactions of organics by hydrogen peroxide. So that, these Ti containing zeolites have been applied successfully in alkene epoxidation, ammoxidation of ketones, phenol hydroxylation and in a number of other processes [13]. These catalysts had proved very active due to their ability to effectively activate the hydrogen peroxide.

Even though the Ti-MFI zeolites turned out to be the most studied because of the best catalytic characteristics in the reactions mentioned above, their structure have rather small pore diameter. This imposes strong diffusion limitations in the case of bulky substrate oxidation.

However, there were no attempts to study systematically both pore diffusion processes in MFI zeolites and their effect on catalytic reaction rates. Also, any attempts to modelling the pore diffusion processes, which occur in the zeolite crystals of various shape in the case of bisubstrate reactions, are lacking in the literature.

Our study was aimed to develop a method for quantitative determination of pore diffusion characteristics of various substrates in nonspherical crystals of titanosilicates, so as to use this approach to evaluate diffusion coefficients for a number of organic substrates.

Titanosilicate catalyst samples were prepared with different size of varying from 0.2 to 30 μm. These samples were tested as catalysts for epoxidation of propene, hexene, cyclohexene and 3-ethylheptene having different size of molecules. On increasing the size of titanosilicate crystals, the noticeable diffusion limitations were found to occur only in the case of large hydrocarbon molecules such as cyclohexene and ethylheptene ones.

The use of starting molecular ratio of peroxide-to-substrate large enough makes it possible to estimate the values of pseudo first order reaction constant. Taking these estimates into account, we applied the model of pore diffusion within nonspherical particles, as it has been developed in [6]. Basing on both kinetic data and the sizes of catalyst crystals, we were enables to determine the values of diffusion coefficients for organic substrates investigated in the pores of MFI titanosilicates.

Besides, we suggested a way to estimate the diffusion parameters and to predict catalytic activity for complex reactions that occur within the pores of catalysts with nonspherical crystal shapes.

Acknowledgments

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T9: Exploring reaction mechanisms

Oral

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Modulated oscillations - a new self-oscillatory phenomenon during CH_4 oxidation over Ni

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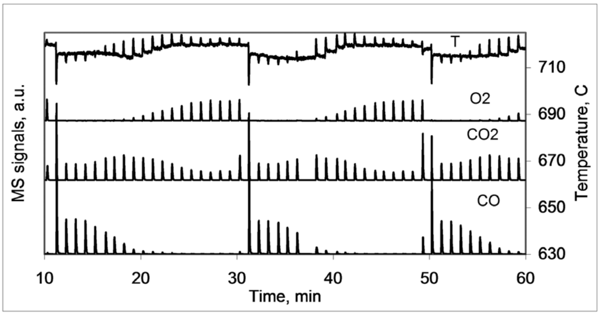
Keywords: Self-oscillations, methane oxidation, nickel catalysts

Introduction
Self-oscillations of catalytic reaction rate is an interesting kinetic phenomenon that allows to reveal in more details a mechanism of the reaction. It was believed that self-oscillations could be observed only for open systems with continuous supply of reactants. We assumed that self-oscillations during some heterogeneous catalytic reaction could be also detected with pulse supply of reagents and the results would give an additional information about the reaction mechanism. Methane oxidation over Ni was selected for the investigation because of well-known self-oscillations under the continuous supply mode.

Materials and Methods
Ni foil sample (4×3×0.5 mm) with an internal thermocouple was prepared from a Ni capillary. Catalytic experiments were carried out in a tubular quartz flow-through reactor. A quadrupole mass-spectrometer (Pfeiffer, OmniStar GSD 301) was employed to analyze the composition of the outlet gas flow.

Results and Discussion
Periodic variations of MS signals related to reagents and products in series of $7.3\%O_2$-$40.8\%CH_4$-He pulses were observed in the range of the Ni foil temperature from 650 to 800°C[1]. The waveform of the periodic variations (Fig.) reminds one of a well-known effect whereby a high-frequency oscillation signal becomes modulated by a low-frequency oscillation signal. Therefore, this phenomenon will be henceforth referred to as "modulated" oscillations with the period equal to the number of pulses between the repetitive responses.

The Ni temperature curve demonstrates that there are at least two types of temperature effects. Temperature effects of the first type are caused by heat evolution during the gas pulse contact with the catalyst. These effects were exothermic or endothermic depending on a selectivity of CH_4 transformation in every pulse. Effects of the second type led to the stepwise changes in the temperature of the Ni foil when in He flow between the reaction mixture pulses. Such step-wise changes were related to changes in heat transfer between the Ni foil



and the surrounding furnace because they occurred when Ni foil changed its color between light metallic Ni and dark NiO.

The pulse experiments allowed more accurate measurements of O- and C-containing gas components and calculations of O and C balances in every pulse. Positive or negative O disbalances in some pulses have proved NiO reduction or Ni oxidation correspondingly in different stages of the oscillation cycle. Similarly, C disbalances revealed the stages with carbon accumulation or removal. The observed selectivities of CH_4 transformation (total oxidation to CO_2 and H_2O, partial oxidation to CO and H_2, decomposition to C and H_2) depended on the oxidation and carbonization degrees in each pulse.

Conclusions

For the first time it has been shown that the self-oscillatory behavior during heterogeneous catalytic reactions can be studied by the pulse method. The pulse method allows to eliminate the influence of heat and mass-transfer effects on the reaction rate and to reveal the role of reactor dynamics in the origin of the self-oscillations. The complicated waveform of the temperature variations during the "modulated" oscillations allowed to distinguish the heat effects from the chemical reaction proper as well as from the heat transfer processes in the reactor-furnace system. The application of the pulse method can “freeze” some of the states of the catalyst during the fast stages of the self-oscillations revealing the fine structure of the oscillation cycle. The detailed structure of the self-oscillation cycle can be described as a sequence of at least five reaction stages. The role of the accumulated carbon and oxygen in the mechanism of methane oxidation over Ni has been revealed. The new results allow to fill in some of the gaps in our knowledge about the mechanism of self-oscillations during methane oxidation thus enabling further mathematical modelling of the process.

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Acknowledgments

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Water oxidation to dioxygen by $Ru(bpy)_3^{3+}$ in the presence of colloidal Fe and Co-hydroxide catalysts. Kinetics study and mechanistic insights

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Keywords: oxygen evolution reaction, oxidation of water, hydroxides, colloids, stop-flow

The development of efficient catalysts for water oxidation reaction (WOR) is a key point to a technology of the solar energy conversion into the energy of chemical bonds. Detail appreciation of WOR kinetics and mechanism is necessary to the design the efficient catalytic systems for this process [1]. The main obstacle to study of kinetic regularities is a short reaction time (of the order of milliseconds). Here we suggest the colloidal Fe-, Co-hydroxide catalysts stabilized by dextranized starch and “stop-flow” method to overcome these difficulties.

The reaction kinetics were registered on two wavelengths (452 and 675 nm) in the most efficient conditions for O_2 releasing. The second order of the reaction was revealed. The observed turnover frequencies were 14 and 60 mol O_2 per [catalyst] s^{-1} for Fe and Co-contained catalysts, respectively. The observed activation energy (278-308 К) appeared to be 10.8 and 11.1 kkal mol^{-1} for Fe- and Co-catalysts, respectively. After consuming of 90 % of $Ru(bpy)_3^{3+}$ we observed the formation of long-lived intermediate on 675 nm. The detailed study by use of LED matrix in vide wavelength range (250-780 nm) revealed that observed intermediate is a product of interaction between catalyst and oxidant (absorbance maximum 550-600 nm). The constant of intermediate consumption was found to be lower by 2-3 orders than the effective constant of oxygen releasing. Thus, the observed compound cannot participate in oxygen releasing reactions. We suggested that observed intermediate is μ-peroxo species on the surface of the catalysts, which are unable to release molecular O_2 but able to oxidize organic ligands of $Ru(bpy)_3^{3+}/Ru(bpy)_3^{2+}$.

Based on the obtained kinetic data we proposed the reaction scheme which include two main routes of $Ru(bpy)_3^{3+}$ consumption – the oxidation of water and the destruction of the organic ligands.

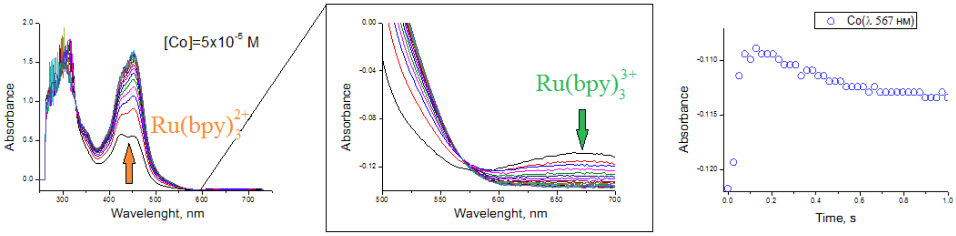

Figure. UV-vis spectrum of WOR in presence of Co-catalyst and intermediate consumption kinetic. $[Co]=10^{-5}$ M, $[Ru(bpy)_3{}^{3+}]=5\times10^{-4}$ M, 0.06 M borate buff., pH 9.2, 298 K.

Acknowledgments

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Operando studies of self-sustained reaction rate oscillations in steam reforming and oxidation of hydrocarbons over nickel

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Keywords: heterogenious catalysis, propane staem reforming, propane oxidation, methane oxidation

Since the discovery of the self-sustained reaction rate oscillations in the catalytic oxidation of CO on platinum metals in 1972 [1], a huge amount of scientific researches was devoted to study this quaint phenomenon. This also initiated a search of other oscillating heterogeneous reactions. As a result, the kinetic oscillations have been discovered in a wide row of catalytic reactions including the oxidation of CO, H_2, and different organic compounds, the hydrogenation of CO and hydrocarbons, NO reduction, N_2O decomposition [2-4]. To date, the oscillatory behavior was observed in approximately 40 heterogeneous catalytic reactions in a wide pressure range from ultra-high vacuum to atmospheric pressure over different types of catalysts. Many researches actively studied this unusual phenomenon using different modern techniques however the reasons initiating the oscillatory behavior are still not clear until now. Here we present the results of our mechanistic study of the self-sustained oscillations in the methane oxidation, the propane oxidation, and the propane steam reforming with added oxygen over nickel foil. The oxidation of methane was studied at atmospheric pressure by X-ray difraction and mass spectrometry. Two other reactions were studied by near-ambient pressure X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, mass-spectrometry, and gas chtomatography in the mbar pressure range. Using this *operando* aproach we simaltateniously studied the catalyst state and products and reactants in the gas phase. The obtained data allowed us to find a correlation between the chemical state and activity of the catalyst and to elucidate the oscillatory mechanism. We found that in all these reactions the self-sustained oscillations originated due to periodical oxidation and reduction of nickel. The high-active state is presented by nickel in the matalic state; the transition to the low-active state is accomponited the growth of a thick NiO film. The first results are published elsewhere [5-7].

Acknowledgments
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Potentiometric scanning electrochemical microscopic mapping of the distributed Belousov-Zhabotinsky oscillating reaction

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Patterns emerging in a distributed Belousov-Zhabotinsky reaction are usually studied with optical methods. However, these methods provide only approximate information about the oxidation state of an indicator, and they cannot be applied when there is no indicator dye or other colored component whose concentration is oscillating. To gather additional information about the processes involved in the reaction, electrochemical methods have been used by many research groups. Unfortunately, these methods will influence a distributed system, since they require electrodes to be placed inside the reaction mixture. The electrodes – depending on their size – will influence the formation of spatial patterns, especially if one of them moves, for instance when used as a measuring tip in scanning electrochemical microscopy (SECM).

The aim of this work is to show that the advantages of optical and electrochemical methods can be combined. That is, spatially resolved electrochemical data can be gathered of certain species in the reaction. Furthermore, we show that, using a sufficiently small indicator microelectrode, convective effects can be minimized to a point where no evidence of any disturbance by the moving microprobe to the reaction can be observed. The first spatiotemporal SECM image about a distributed Belousov-Zhabotinsky reaction is shown, overlayed on top of the corresponding optical spatiotemporal image.

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Realizations of generalized mass action systems and their use in stability analysis

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Keywords: generalized chemical reaction networks, realizations, dynamic behavior, kinetic phenomena

Generalized mass action systems in the sense of [1] are able to capture the structure and dynamic properties of chemical reaction networks even in intracellular environments. It has been shown that several results of chemical reaction network (CRN) theory carry over to the case of generalized mass action kinetics. It is known, however, that the most important properties of CRNs, including their deficiency, reversibility and balancing, are realization-dependent.

Therefore, one of the aims of this work is to extend the optimization-based computational tools available for CRNs [2] to the case of generalized mass action systems, and to investigate their use for stability analysis of such systems.

On the other hand, quasi-polynomial or generalized Lotka-Volterra systems has been recognized as a related class of generalized mass action systems, for which efficient stability analysis tools are available [3]. A recent paper [4] gives the first results relating generalized Lotka-Volterra and mass action models for stability analysis. Based on the realization theory of generalized mass action systems we aim at giving more general results in this direction.

Acknowledgments

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Mechanism and kinetics of hydrogen peroxide decomposition on platinum nanocatalysts

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Keywords: mechanism, platinum nanocatalysts, kinetics

The disproportionation of hydrogen peroxide (H_2O_2) to water (H_2O) and molecular oxygen (O_2) catalyzed by platinum (Pt) nanocatalysts is technologically very important because it affects the energy yield generated in hydrogen fuel cells and steam propellers with application in spacecraft or underwater vehicles. Despite its importance, the reaction pathway of H_2O_2 decomposition on Pt catalysts has been an unresolved question for more than 100 years. New studies are needed to develop a molecular scale understanding of the reaction mechanism and kinetics. To this end, we characterized two Pt nanocatalysts and studied the effect of different reaction conditions on their rates of H_2O_2 decomposition. Our goal was to determine the reaction pathway and understand the kinetics of H_2O_2 decomposition on Pt nanocatalysts.

Rate measurements were performed using two Pt nanocatalyst samples with average particle sizes *(d)* of 11 nm (Pt-11nm) and 23 nm (Pt-23nm). The effect of surface oxidation was evaluated by heating both Pt nanocatalysts at 240 °C for 24h in air, which causes chemisorption of oxygen onto the surface of Pt. The effect of particle size was evaluated by combining our results with six additional data points published in literature for a Pt nanocatalyst sample with particle size of 3 nm (Pt-3nm)[1]. Multi-variate linear regression analysis was used derive the rate equations and compare the catalytic activity of H_2O_2 decomposition as a function of $C_{H_2O_2}$, pH and temperature *(T)* between the three nanocatalysts.

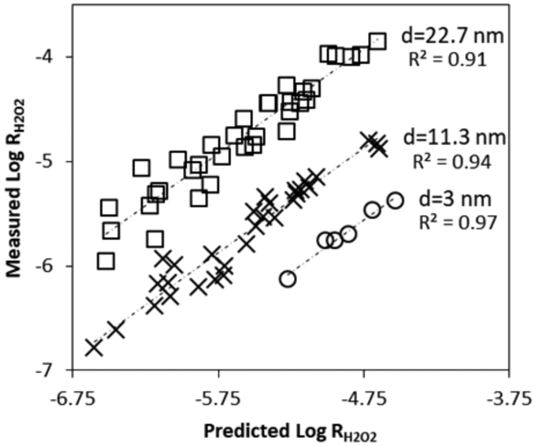

Figure 1. Regression model of log measured R vs log predicted R for Pt-23nm (□), Pt-11nm (x) and Pt-3nm (○) as function of $C_{H_2O_2}$, pH and 1/T.

H_2O_2 concentration and pH affected the activity of all three nanocatalysts similarly. Larger particle size values correlated with enhanced catalytic activity (Figure 1), which is consistent with a 20% lower activation energy determined for Pt-23nm compared to Pt-11nm (p-value=0.01). The particle size effect is explained by a smaller work function for larger Pt particles, which causes oxygen to react faster with surface Pt atoms to form Pt(O). Our experiments also showed that incorporation of oxygen at the nanocatalyst surface resulted in higher catalytic activity because the rate limiting step is skipped in the first cycle of reaction. Taken together, these results indicate that the decomposition of H_2O_2 on Pt proceeds by cyclic chemisorption of oxygen onto surface Pt to form Pt(O), followed by reduction of Pt(O) back to Pt, releasing a second molecule of water and molecular oxygen (reaction 1-3). These results also showed for the first time that step 1 is the rate limiting step of the reaction.

$$\text{Step 1} \qquad \boldsymbol{Pt + H_2O_2 \rightarrow H_2O + Pt(O)} \qquad (1)$$

$$\text{Step 2} \qquad \underline{Pt(O) + H_2O_2 \rightarrow Pt + O_2 + H_2O} \qquad (2)$$

$$\text{Overall} \qquad 2\,H_2O_2 \rightarrow O_2 + 2H_2O \qquad (3)$$

The knowledge developed in this study will help redesigning Pt nanocatalysts to improve the efficiency of important energy conversion technologies, such as hydrogen fuel cells and steam propellers.

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Computational generation of reaction schemes with complex dynamics

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Keywords: chemical reaction networks, nonlinear dynamics, oscillations, computational methods

Kinetic systems are dynamic models the behaviour of which can be formally described by a chemical reaction scheme (i. e., by a chemical reaction network). Such models form a wide subclass of non-negative polynomial systems with increasing research interest both from a theoretical and from a computational point of view [1]. Kinetic models are often used to model the dynamical behaviour of physico-chemical systems, complex networks appearing in systems biology, temporal ecological systems, transportation processes, compartmental systems or disease spreading. The main reason for this is that the dynamical descriptive power of chemical reaction networks is good, i. e. they are suitable for modeling complex dynamical phenomena like the multiplicity of equilibria, limit cycles, oscillations or even chaotic behaviour. On the other hand, the simple algebraic structure of kinetic models containing information both on the stoichiometry and the graph structure in a very transparent way make it particularly appealing to study their properties in a computational framework. The literature of chemical oscillations is really huge with detailed chemical and mathematical analysis of several well-known experimental and related abstract theoretical examples such as the Belousov–Zhabotinsky reaction, the Briggs–Rauscher reaction, the Brusselator, or the Oregonator [2].

It is well known that the reaction graph corresponding to a set of kinetic ordinary differential equations is non-unique. In [3], we gave a computational method for generating all possible reaction graph structures corresponding to a kinetic dynamics when the parameters of the dynamical model are assumed to be exactly known. In this contribution, we introduce the extension of this approach to handle entire sets of reaction rate coefficients. The approach is based on the iterative solution of optimization problems, where the constraints containing the rate coefficients ensure the kinetic property (i. e., the realizability by chemical reactions) and the complex dynamical behaviour at the same time. In the case of certain models, it is possible to enumerate all structurally distinct reaction schemes leading to the same oscillating dynamics, assuming a fixed set of chemical complexes. Moreover, the theoretical correctness of the reaction scheme generating method can also be proved.

Acknowledgments

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Parahydrogen enhanced NMR studies of metal-free H_2 activation by ansa-aminoboranes

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Keywords: metal-free catalysis, hydrogen, ansa-aminoboranes, NMR, hyperpolarization

The potential of metal-free catalysis based on the concept of a frustrated Lewis pair (FLP) has attracted considerable attention. Meanwhile, the ability of some FLPs to activate H_2 is of significant interest for sensitivity enhancement in NMR spectroscopy and MRI. The activation of H_2 is the key element of parahydrogen-induced polarization (PHIP), one of the nuclear spin hyperpolarization techniques. Recently, it has been demonstrated that ansa-aminoboranes (AABs) [1,2] can produce ^{1}H nuclear spin hyperpolarization through a reversible interaction with parahydrogen at ambient temperatures.[3] Herein, we present our studies on investigation of H_2 activation by AABs of different structures.[3-5] The chemical mechanism aspects are discussed through the coupling to nuclear spin dynamics and observation of strong NMR signals enhanced by the use of parahydrogen as a reagent.

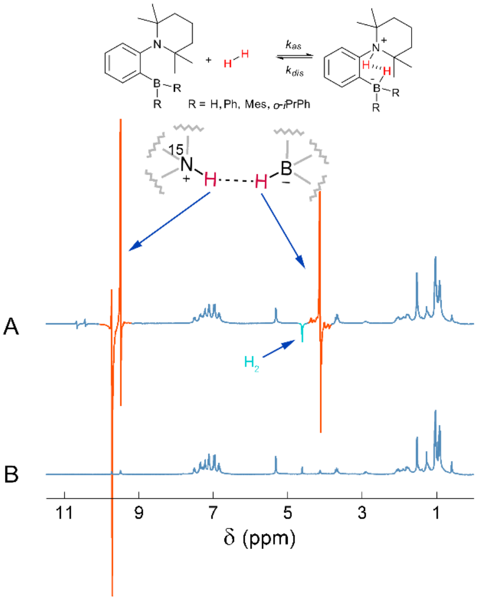

Figure 1. (A) Enhanced ^{1}H NMR signals observed after metal-free activation of parahydrogen molecules. The signals corresponding to parahydrogen originating hydrogens have antiphase shape and high intensity. (B) ^{1}H NMR spectrum observed when normal hydrogen is used.

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Kinetic model of thiol-en reaction of glutathione with unsaturated phenols

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Keywords: glutathione, kinetics, resveratrol, caffeic acid, thiol-en reaction, hydrogen peroxide

Natural endogenous thiol glutathione (GSH) is known to perform a variety of antioxidant functions by interacting with hydroxyl radicals, reducing hydroperoxides, and disulfide bonds –S-S-, preventing oxidation of proteins. The physiological content of glutathione in biological fluids is high enough (up to 10mM). and it exists in two forms: reduced (GSH) and oxidized (GSSG). In some cases it is regarded as a biomarker for some clinical situations and diseases such as Alzheimer's, Parkinson's, rheumatoid arthritis and cardiovascular diseases. A special role belongs to glutathione in the maintenance of intracellular redox balance.

trans-Resveratrol (RVT, 3,5,4´-trihydroxystilbene) is known as phytoalexin, which is presented in grapes and red wines in relatively large amounts. Caffeic acid (CA) similar to RVT is known as having immunomodulatory and anti-inflammatory activity and the inhibitory effect on cancer cell proliferation and having in molecule double bond conjugated with phenolic ring.

We have studied the kinetics of reducing H_2O_2 by GSH in detail and found that this reaction is accompanied by free radical formation [1]. The yield of radical is low (~0,3%) but it is enough for initiation of thiol-en reaction between resveratrol and caffeic acid with glutathione [2]. Thiol-en reactions are of great interest in medical chemistry for synthesis of new drugs because they result in formation of new hetero-compounds [3,4].

This study presents a kinetic model of the interaction between unsaturated phenols (RVT and CA) with GSH in aqueous medium at physiological temperature 37°C. The interaction occurs via free radical chain mechanism, where thiyl radicals are initiated in the reaction of GSH with H_2O_2. Chain termination occurs via fast recombination of thiyl radicals, the corresponding rate constant was determined by flash-photolysis method. The other main rate constants are determined from experimental data on reagent consumption. Computer simulation was used to compare the calculated and experimental kinetic curves for reagent uptake in reaction of GSH with RVT and CA and for the definition of the missing kinetic parameters. The obtained results can be useful for understanding the physiological role of thiols in oxidative processes.

Acknowledgments

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Poster

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New oscillating system: CO oxidation over Ni

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Keywords: self-oscillations, CO oxidation, nickel catalysts

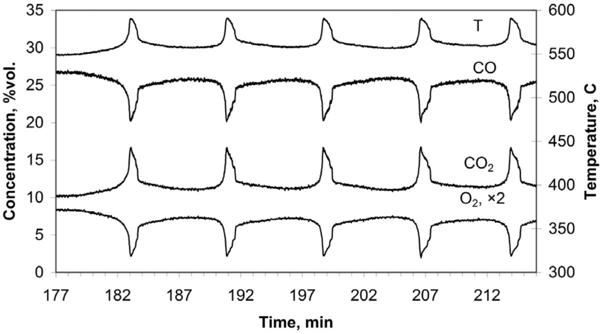
Introduction

The very rich dynamic behaviour observed in many heterogeneous catalytic reactions including spatiotemporal patterns and self- oscillations have been a subject of considerable research activity within the past few decades. Self-oscillations in a heterogeneous catalytic CO oxidation were observed on Pt, Pd, Ir, Rh, and Ru catalysts. Surprisingly, the oscillatory behavior during CO oxidation over Ni catalysts has not been observed yet. The most studied oscillating reactions over Ni catalysts are H_2 oxidation and CH_4 oxidation. The application of in-situ methods indicated that the origin of the oscillations was connected with the periodic reduction and oxidation of Ni. The results obtained demonstrate that during the self-oscillations of CH_4 oxidation rate, the surface of the nickel catalyst contained a considerable amount of carbon which can take part in the feedback mechanism. In contrast to CH_4 oxidation, the mechanism of catalytic CO oxidation over metals does not include stages characterized by surface carbon formation. Therefore, a study of oscillatory CO oxidation can reveal the role of oxidation-reduction processes of Ni in the dynamic behavior of the system.

Materials and Methods

Ni foil sample (4×3×0.5 mm) with an internal thermocouple was prepared from a Ni capillary. Catalytic experiments were carried out in a tubular quartz flow-through reactor. The reactor was inserted into a furnace which allowed observation and recording of the state of the sample surface by a photo-video camera Canon EOS 70D. A quadrupole mass-spectrometer (Pfeiffer, OmniStar GSD 301) was employed to analyze the composition of the outlet gas flow.

Results and Discussion



Regular oscillations during CO oxidation[1] over the Ni foil were observed in the temperature range 570-630 °C for the reactant mixture containing 40% CO and 10% O_2 in He. Fig. demonstrates the oscillations of the gas phase concentrations and Ni temperature variation at furnace temperature of 570 °C. An increase in temperature led to a decrease in the period of the oscillations. At temperatures of 610-630 °C the oscillatory behavior became irregular. The oscillations occurred as transitions between states of lower and higher activities. A large peak of positive oxygen imbalance observed during the transition from the low to the high oscillation activity branch points to fast reduction of NiO. After this sharp peak a slow increase in slightly less intensive negative imbalance was observed. This part of the oscillatory cycle corresponded to the process of Ni oxidation and the related decrease in the reaction rate was detected.

The reaction rate oscillations were accompanied by synchronous variations of color changes of the Ni foil. The propagation rate of the oxidation wave is nearly 10 times lower than the rate of the reduction wave. Moreover, the reduction wave propagation rate tends to increase with temperature, while the front forward motion of the oxidation wave decreases with the temperature increase.

Conclusions

For the first time, the oscillatory behavior during CO oxidation over Ni foil has been discovered. The oscillatory behavior occurred in CO excess in contrast to the well-known oscillations during CO oxidation over Pt, Pd, Ir, and Ru. The periodic variation of oxygen imbalance together with the variation of color changes during the oscillations indicated that the oscillations were closely connected with the reversible oxidation of Ni to NiO. The observation of oscillations in a pulse supply mode proved their kinetic origin. The oscillations were accompanied by the propagation of the oxidation and reduction fronts which could be observed with the naked eye.

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Acknowledgments

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A computational and conceptual DFT study on the mechanism of producing 3,8-dimethyl-3H-imidazo[4,5-a]acridine-11-carbonitrile

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Keywords: DFT study, electrophilic mechanism, NBO calculation, imidazo[4,5-a]acridine

Results and discussion

Nowadays, it is demonstrated that Imidazo Acridine derivatives considerably noted for the synthesis of drugs for treatment many diseases[1], other aspects of industrial organic material's usage[2-4] and some valuable drugs[5]. In spite of increasing attention to the synthesis of these compounds[6], have no evidence of theoretical study to their mechanism, especially in one-pot synthesis.

In this paper, the best mechanism of producing 3,8-dimethyl-3H-imidazo[4,5-a]acridine-11-carbonitrile has been theoretically investigated in gas phase and methanol in detail. Solvent effect, activation energy and free Gibbs energy for all steps were calculated by employing DFT, the B3LYP[7-9] hybrid density functional level, 6-311++ G(d, p) basis sets and the PCM model using the Gaussian 03 package[10].

Related thermodynamic quantities collected in Table 1 were obtained at room temperature and 1 atm. pressure for giving exact conditional on the experimental results6.As can be seen on Scheme 2, two paths are available, path II has three steps: tautomerization, cyclization and losing H_2O, while path I just has two steps. Energy profile for the mechanisms of the reaction, will be coming in Fig.7.

For the path I were supposed, may be tautomerization lead to cyclization simultaneously as well, but it has higher activation energy than all reactions related to Path II therefore path I is rejected (Fig.1). Obviously, the plot of Fig.1 shows, reaction B-C14 or B-C12 is possible. The angle of C4-C7-C8 for all enol forms increased via tautomerization as well as bond length of N4-O1, but the length of C8-C7 and C7-C4 were decreased (Table 2).

All results about activation energies for two paths will be coming in Table 3, Fig.2.

Solvent effect decreases Eact by 9.08 for TSBD by kJ/mol. In the first step of Path II, four configurations of C species were possible (Scheme3). All related activation energies were computed in the gas phase and methanol as a polar solvent (Fig.3, Table 3). However, considering the solvent effects in the tautomerization prefers methanol phase 6.38, 8.96, 6.51, 10.79, 9.08 by kJ/mol for B–C11, B–C12, B–C13, B–C14 and B-D, respectively.

In the solution, C14 is more stable than others, while B form is the most stable, in both phases.

By comparing the activation energies for all possibilities of tautomerization, can be concluded that there is a possibility for B–C12 or B–C14 reactions by just 2 kJ/mol differences in methanol phase.

By considering supposed four mechanisms (Scheme 4), may be happened in the cyclization step, B–D was rejected in the previous section (Scheme2). Optimized structures are shown in Fig.4.

Obviously by comparing results, in the methanol, the Eact's have increased 13.66, 0.66, 14.17, 0.47 by kJ/mol for C12D, C14D, C12G and C14G, respectively (Table 4, Fig.5). Results shows that reaction C12–G is possible.

It means, the mechanism of cyclization is Electrophilic. The NBO calculation[11-12] shows that there is interest C3 (not C5) to start attaching to N4 because of more partial negative charges (Table 5).

The final step, is the rate-determining step because of the highest Eact (Scheme 5).

The solvent effects decreased Eact, by 10.24 and 7.12kJ/mol for producing from D or G, respectively (Fig.6).

Conclusion

The computed Eact, reveal that the major path for producing E, is the Pathway II (Fig.7) B-C12-G-E.

Additionally, by considering NBO data can be proved Electrophilic mechanism for cyclization step as well. This finding is consistent with previous experimental studies.[6] Moreover, by considering activation energies for all steps, it could be clearly understood that losing H_2O for Producing E, is the rate-determining step.

Results shows that decreasing activation energy for the tautomerization and final step, while for the cyclization step, activation energy were increased. All figures, tables & schemes are available.

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