

Sustainable Oxidation Catalysis for Synthesis

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Abstract

At present, many oxidation reactions rely on inefficient and wasteful methods that are problematic on a larger scale. There is a need to develop efficient catalysts that use sustainable terminal oxidants such as molecular oxygen or hydrogen peroxide. Although such methods are employed in the preparation of commodity chemicals, they are rarely used for the synthesis of fine chemicals, agrichemicals or pharmaceuticals. The Muldoon Group has been focused on developing catalysts for a number of different oxidation reactions, including alcohol oxidation, Wacker type oxidations and oxidative synthesis of nitriles. In this talk we will discuss the challenges in this area and our recent work, exploring palladium, copper and metal-free catalytic methods.

Mechanistic Insights into Cu(II) Catalyzed Diels-Alder Reactions by EPR Spectroscopy and Calculations

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Abstract

The geometry of several catalytically-active Cu(II) complexes (particularly with bis(oxazoline) ligands) is rather well established by X-ray crystallography.

However what happens in the course of the catalytic reaction? Such reactions are usually performed in solution and the solvents together with the counterions substantially influence the efficiency of these reactions (1).

It is unfortunately hardly possible to crystalize reaction mixtures during the reaction. Since Cu(II) is paramagnetic, EPR and related spectroscopic methods can be utilized to investigate the geometry of the complexes during the catalytic reaction. With the insights obtained by spectroscopy, the environment around Cu(II) can be modelled by DFT calculations.

The lecture will summarize our results in this field (2-5).

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Catalytic and photocatalytic reactions on oxygen-isotopes labeled titania

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Abstract

Titania catalysts labeled by oxygen isotopes 16, 17, 18 were synthesized, each in anatase and rutile forms. The products were characterized by Raman spectroscopy and by Raman spectroelectrochemistry of Li-insertion. [1]. The second-order Raman scattering in rutile, and the overlapping Raman features in anatase were addressed in detail. [2] The Ti^{17}O_2 is of interest for EPR studies, due to the nuclear spin of ^{17}O . [3] The heterogeneous catalytic processes at the interface of titania and gaseous reactants were investigated by high-resolution FTIR spectroscopy in dark and upon UV-excitation [4-6]. The vacuum-annealed Ti^{18}O_2 exhibited high oxygen-exchange activity with C^{16}O_2 . The dominating final product of the oxygen isotope exchange at the $\text{Ti}^{18}\text{O}_2(\text{s})/\text{C}^{16}\text{O}_2(\text{g})$ interface was C^{18}O_2 with small amount of $\text{C}^{16}\text{O}^{18}\text{O}$. The UV photocatalytic formation of methane, acetylene and C^{16}O was studied at the Ti^{18}O_2 modified by adsorbed H_2O and HCl . Compatible data were acquired for photocatalytic and catalytic processes of formic acid [5] and COS [6] at the Ti^{18}O_2 surface. The disproportion of OCS to CO_2 and CS_2 is catalyzed by Ti^{3+} centers on the partly doped titania. [6] Formic acid did not exchange oxygen with titania during adsorption and decomposition processes, but blocked active sites and thereby inhibited the exchange between CO_2 and Ti^{18}O_2 . Similar blocking was observed by adsorbed water.

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Solar Photocatalysis, overview and applications

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Abstract

Conventional wastewater treatment plants are not effective when wastewaters have to be treated due to the high COD load and the presence of recalcitrant compounds. An alternative to conventional water treatments are Advanced Oxidation Processes (AOPs) which are able to oxidize almost any organic molecule, yielding CO₂ and inorganic ions. The versatility of the AOPs is enhanced by the fact that there are different ways of producing hydroxyl radicals, facilitating compliance with the specific treatment requirements. Several promising cost-cutting approaches have been proposed based on a integration of the AOP as part of a whole treatment train or process. Other proposed cost-cutting measures are the use of renewable energy sources, i.e. sunlight as irradiation source for TiO₂ photocatalysis and photo-Fenton. Therefore, low cost solar AOPs systems suitable to be combined with biological processes are innovative options in this area. The solar approach is a logical consequence for AOP cost saving to be applied especially in the Southern Europe regions.

Post-treatments can be used as polishing step after a biological treatment in the case of wastewaters containing large amounts of biodegradable organics and small concentrations of biorecalcitrant compounds, as effluents from municipal wastewater treatment plants (MWTP). Pre-treatments can be advisable in the opposite case, i.e. when the amount of bioresistant toxic contaminants is greater than that of biodegradable matter, a typical situation found in many industrial wastewaters. This work will overview not only the main solar AOPs (TiO₂ photocatalysis and photo-Fenton) but their application in the treatment of industrial wastewaters containing conventional contaminants and effluents from MWTP containing micro-pollutants and ECs, forming part of a complete treatment chain for optimising treatment costs. Solar photocatalytic disinfection and production of hydrogen by solar photocatalysis will be also highlighted.

Liquid phase hydrogenations over dispersed metal catalysts

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Abstract

Liquid phase hydrogenations have their peculiar features due to mass transport hindrance and a higher attack on catalytic centres than in gas phase processes. Slurry systems with dispersed metal catalysts are preferred to minimize these phenomena and consequences for reaction rate, selectivity, deactivation and other process parameters. This contribution is devoted to catalytic and technological aspects of the following processes (main catalytic metal is indicated in brackets): (i) removal of nitrates from potentially drinking water (palladium), (ii) selective reduction of benzene to cyclohexene (ruthenium), (iii) aniline from nitrobenzene (palladium), (iv) cyclohexylamine from aniline (ruthenium), (v) 4-aminodiphenylamine from 4-nitrodiphenylamine and 4-nitrodiphenylamine (palladium) in the presence of a strong base. Hydrogenability of a substrate, reaction routes determining selectivity, choice of metals and procedure of catalyst preparation, reaction conditions and changes of catalysts including deactivation are matters of discussion. A special focus is on the effect of water.

Besides importance of a proper mathematical description of mass and heat transport phenomena and complex reaction kinetics, the inevitable role of experimental modeling is stressed. Model units, which are more than ten times larger than common laboratory equipment, have proven to be a very powerful tool for design of technologies.

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Enantioselective cascade reactions catalyzed by chirally modified metal surfaces

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Abstract

Recent modern methods developed for the preparation of optically pure chiral fine chemicals include one-pot asymmetric catalytic cascade reactions, which beside multiplication of chirality also spare the laborious and costly isolation and purification of intermediate products. Increasing efforts were also oriented to the use of heterogeneous asymmetric catalytic systems, due to strict requirements of applying environmentally friendly and sustainable procedures. Combining these approaches led to the development by our research group of few enantioselective heterogeneous cascade reactions catalyzed by supported metal catalysts modified by optically pure compounds, such as Pt or Pd modified by cinchona alkaloids. The main characteristic of these reactions is that the asymmetric step of the cascade, which is the enantioselective hydrogenation of a prochiral group, occurs on the chiral surface. These asymmetric cascade reactions will be presented, their mechanism and their scope will be discussed and future prospects will be given.

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How to efficiently promote catalytic materials with alkali – understanding the electronic and structural functionalization

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Abstract

Alkali metal compounds are widely used as promoters in many catalytic processes. The addition of alkali affects the catalysts efficiency in many ways by increasing the activity, selectivity or prolonging the lifetime. Although, the beneficial role of alkali additives is experimentally well established in catalysis, a more in-depth understanding of their action is still lacking. This is mainly due to the diversity of the effects caused by the alkali promoters, their high reactivity, surface and bulk mobility, and difficulties in characterization of their real surface states. In an attempt to elucidate the promotional effects of alkali and identify the decisive parameters responsible for their performance a Species Resolved Thermal Alkali Desorption method has been developed. In tandem with work function measurements it provides a powerful tool for the static and dynamic description of the alkali promoters in catalytic systems. The measurements may be conducted in both vacuum and in near-catalytic conditions to bridge the material and pressure gap. Several aspects of alkali doping will be addressed such as surface states, electronic and structural effects, surface spreading, bulk and surface diffusion, and promoter loss via thermal desorption. Each of these issues will be illustrated with results referring to well-defined surfaces of active phases, as well as model and industrial catalysts.

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Advanced nanoarchitecture of iron and iron oxide based materials for environmental, catalytic and biomedical applications

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Abstract

Iron and its compounds show a huge potential in various nanotechnologies owing to their low-cost, biocompatibility, non-toxicity, biodegradability, and environmentally friendly character. The broad scale of accessible valence states (0, II, III, IV, V, VI) and polymorphism of iron(III) oxide [1] contribute to the miscellaneous chemistry and quite unique portfolio of applications of Fe-bearing nanomaterials. In particular, nanoscale zero valent iron (nZVI, Fe^0) is viewed as an environmentally friendly tool for in-situ reductive treatment of ground water and surface water contaminated by, e.g., chlorinated hydrocarbons, uranium, heavy metals, or cyanobacteria [e.g., 2,3]. In the talk, selected results of surface nanoarchitecture and remediation with nZVI will be discussed.

Nanocrystalline iron (II,III) oxides in various structural forms have been found promising materials in biomedicine, biotechnologies, catalysis, photocatalysis of water or many magnetism-based applications. The control of the structural, morphological and surface properties of nanocrystalline iron oxides towards tailored applications in targeted drug delivery and MRI contrast enhancement [e.g. 4], catalysis, and direct solar splitting of water [e.g. 5] will be presented. The extraordinary efficiency of arsenic removal through its embedding in the structure of the in-situ formed magnetic iron(III) oxides will be also presented [6].

The last part of the talk will be devoted to various multifunctional hybrids of iron/iron oxides with carbon nanostructures (graphene, mesoporous carbon, carbon dots) and nanosilver with an emphasis on their applications in advanced water treatment technologies, antimicrobial treatment, heterogeneous catalysis and biomedicine [e.g., 7-9].

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Ultrathin Films of Zirconium Oxide and Cobalt Oxide as Model Catalyst

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Abstract

Solid Oxide Fuel Cells (SOFCs) are promising devices for effective energy generation. Nevertheless, improvements of their performance rely on a fundamental understanding of their components. In order to model SOFC anodes well-ordered ultrathin films of ZrO_2 were grown in ultrahigh vacuum (UHV) by oxidation and annealing of Pt_3Zr or Pd_3Zr single crystals [1]. Ni was then deposited by physical vapor deposition. Ni particles supported by ZrO_2 are widely used in the field of heterogeneous catalysis, such as for reforming reactions.

Cobalt oxide is a highly active heterogeneous catalyst for e.g. low temperature CO oxidation and holds potential for replacing noble metals and/or rare earth oxides. Nevertheless, the origin of the high cobalt oxide activity is still not well explained. Thin cobalt oxide films with well-defined structure were grown on Ir(100) single crystal by Co physical vapor deposition in O_2 background with subsequent post-oxidation [2].

For both systems, the chemical composition of the model oxide was examined by high resolution X-ray Photoelectron Spectroscopy (XPS), the structure was characterized by Scanning Tunneling Microscopy (STM). Water, CO and CO_2 were used to probe the chemical properties of the oxide-films and deposited metal nanoparticles, studied at near ambient pressure by AP-XPS and polarization modulation infrared reflection-adsorption spectroscopy (PM-IRAS).

Oxidation and annealing of the Pt_3Zr (0001) alloy substrate produced a well-ordered and ultrathin trilayer ZrO_2 film. Apart from the planar film, ZrO_2 clusters were identified by XPS depth profiling and STM. Thermal Desorption Spectroscopy (TDS) using CO as probe molecule was then utilized to demonstrate that the entire substrate was covered by the zirconia thin film. The interaction of ZrO_2 with water was examined by synchrotron AP-XPS (Lund). Surface defects, likely oxygen vacancies, created by soft sputtering, induced water dissociation, which was also enhanced at higher water pressures (low mbar range).

For cobalt oxide, 6 ML thick Co_3O_4 (111) or CoO (111) films were prepared. The state of the active component and the interaction with CO, CO_2 and gas mixture ($\text{CO}+\text{O}_2$) with different surfaces of cobalt oxide was examined in the range 200 K – 470 K and from UHV to 100 mbar. Upon CO exposure, carbonates and elementary carbon were observed, in addition to a partial reduction of cobalt oxide even at UHV conditions at room temperature.

For both systems, the model oxides will be compared to corresponding high surface area (powder) catalysts.

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The stability and energetics of the cerium doped anatase and brookite phases – a first-principles study

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Abstract

In cerium doped TiO_2 nanostructured materials prepared by sol-gel technique and thermally treated the presence of Ce ions stabilizes the anatase phase and inhibits its transformation to rutile phase. However, by using pressurized and supercritical fluids the mixture of anatase and brookite phase being prepared instead of anatase phase and even the same Ti:Ce molar mixture (e.g. 70:30) crystallizes differently compared to that thermally treated (the mixture of TiO_2 anatase and cubic CeO_2 phase crystallizes instead of the monoclinic CeTi_2O_6 phase). In order to reveal the cause of different structure crystallizing under pressure, the effect of the addition of Ce on the enthalpy of formation (H_f) for selected Ce concentration in anatase and brookite phases are investigated. The stability of the Ce doped anatase and brookite is compared with the H_f of cerium titanates, e.g. CeTi_2O_6 and CeTiO_4 . Ce site preference (interstitial sites, antisite sites) was determined. The results were obtained by means of the first-principles calculations using the density-functional theory.

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Advantage of single pellet string reactor for testing of real-size industrial catalysts

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Abstract

Two tubular laboratory reactors: single pellet string reactor (i.d. = 0.55 cm) and fixed bed reactor (i.d. = 5 cm) were compared on the basis of laboratory experiments of N₂O catalytic decomposition and measurements of residence time distribution curves. K/Co₄MnAlO_x mixed oxide in the form of cylinders (5.1 mm-width, 5.1 mm-height) was used as a catalyst. The influence of external diffusion, deviation from plug flow and influence of axial dispersion on N₂O conversion obtained in both reactors were discussed. Influence of macroscopic phenomena on the rate of catalytic reaction was significantly lower in single pellet string reactor, which predetermined it as suitable laboratory reactor for testing of real-size industrial catalysts. Experimentally obtained results were confirmed by mathematical modeling.

Keywords: Single pellet string reactor, Fixed bed reactor, External diffusion, Axial dispersion, Peclet number

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Enhancement of activity and selectivity in acid-catalyzed reactions by dealuminated hierarchical zeolites

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Abstract

This paper overviews our recent results on the enhancement of activity and selectivity in acid-catalyzed reactions by using partially dealuminated micro-mesoporous zeolites [1]. Zeolite micropores govern the shape-selectivity effects of the inner reaction space but also implicate slow transport of reactants and products limiting the reaction rate. The advantage of the presence of mesopores for reactant transport is, however, accompanied by the non-shape-selective environment of the acid sites located in mesopores. Partially dealuminated hierarchical mordenite and ZSM-5 zeolites were prepared by treating of conventional zeolites in alkaline solution and subsequently in solution of oxalic acid. Zeolites were characterised by XRD, N₂ adsorption at -196 °C, HR TEM, SEM, ²⁷Al and ²⁹Si MAS NMR, XPS and FTIR spectroscopy of adsorbed *d*₃-acetonitrile and 2,6-ditertbutylpyridine. The hierarchical shape-selective zeolites provided unprecedented high yields of the desired products in the representative acid-catalyzed reactions as a result of synergism of the enhanced rate of reactant/product transport and presence of acid sites in the shape-selective confined space of the micropores. The potential of these hierarchical zeolites is demonstrated on hydroisomerization of n-heptane, cracking of n-hexane and acylation of anisole with acetic anhydride to p-methoxyacetophenone.

Acknowledgement

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Electrochemical behaviour of amino acids on thin layers of ZnO prepared by ink-jet printing

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Abstract

The solid-phase interface behaviour under contact with various electrolytes plays the key role in understanding of physicochemical processes occurring on the surface. Especially the surfaces of various semiconductors are studied for their potential utilization as sensors or actuators. The systems involving semiconductors surfaces and electrolyte solutions possess very complex processes on atomic scale. Among many physical processes involved, the hydrodynamic processes and diffusion of species are of greatest interest. A small perturbation induced by the concentration change of electro-active species or gradient of temperature can cause a very sharp change in electrochemical behaviour on the interface.

The standard system worked with thin layers of ZnO on ITO glass deposited by ink-jet printing. As electrolyte 0.1M Na₂SO₄ solution with various concentration of amino acids (glycine, glutamic acid, aspartic acid, histidine and methionine) was used. The electrochemical behaviour was tested by Open Circuit Potential measurement. A kinetic study of involved electro active species was expressed.

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Printed thin layer photocatalytic dosimeter

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Abstract

Almost one half of human population suffers from vitamin D insufficiency. This vitamin is possible to be supplied by food and drugs but the most natural source of vitamin D is the irradiation of skin by UV-B light (290–320 nm). On the other hand, UV-B light is the strongest carcinogenic component of natural sun radiation. A solicitous monitoring of body exposure in various situations is a required information for targeted dosing of phototherapy and also for an appropriate application of photo protective precautions – use of clothes and sunscreens. Patients with heavy photosensitivity need the means of personal warning dosimetry. Such dosimeter should be sensitive to UV-B radiation and reveal information about exposure dose through substantial colour change. In fact, optimally it should work as a memory element which transforms the continuous time axis to the cumulative form with any required precision. The sensing elements was completed on the basis of photochemical and photocatalytic principles with auxiliary components. The dosimeter consisting of dispersed titania particels, dyes, solvents and additives was printed using roll-to-roll material printer on a polyethylene terephthalate foil. Suitable dyes selections for printed dosimeter were based on spectrophotometric measurements of thin printed layer of dosimeter. Radiometric calculations necessary for such printed dosimeter calibration will be also presented.

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Surface activation of mesoporous ordered silica materials by aluminum and cobalt, their characterization and catalytic activity for N₂O decomposition

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Abstract

Three different mesoporous ordered silica materials such as MCM-41, MCM-41 with grafted and incorporated aluminum and SBA-15 were prepared by the molecular designed dispersion method (MDD). In further step, cobalt (1-16 wt%) was used as an active transition metal for the catalytic reaction of N₂O decomposition. The possible interaction of acetylacetonate complexes as precursors with support surfaces by hydrogen bonding versus ligand exchange mechanism were tested by infrared spectroscopy and thermogravimetric analysis. Prepared catalysts were characterized by nitrogen sorption, electron-probe microanalysis, energy dispersive X-ray analysis, X-ray diffraction, scanning electron microscopy, UV-vis-DR spectroscopy, temperature programmed reduction of hydrogen and temperature programmed desorption of ammonia. The N₂O conversion slightly increased with the higher content of aluminum. The role of different supports influencing the properties of active sites created by cobalt ions is discussed.

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Catalytic and non-catalytic photochemical degradations of aniline and nitrobenzene in industrial waste waters: comparison of process parameters

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Abstract

Metal phthalocyanines in the presence of visible light are applied in the semi-pilot level for the degradation of organic pollution represented by nitrobenzene and aniline with potential further scale-up. The effectiveness of the process based on the generation of singlet oxygen active species is compared with commonly used method of photochemical oxidation with hydrogen peroxide in the presence of ultraviolet irradiation. The direct comparison of the reaction systems was conceivable because both oxidation processes were carried out in identical experimental arrangements and under identical reaction conditions. The comparison was performed in terms of nitrobenzene and aniline conversion, TOC removal, apparent quantum yields, kinetic constants, and economy considerations.

Acknowledgement

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WO₃ and α -Fe₂O₃ films for photo-electrochemical water splitting

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Abstract

Iron oxide (α -Fe₂O₃) in hematite crystalline structure and tungsten trioxide have recently attracted much attention as possibly convenient materials to be used for hydrogen production via photoelectrochemical water splitting. It is due to their favorable properties such as band gaps between 2.0 - 2.2 eV (α -Fe₂O₃) and 2.5–2.8 eV (WO₃) which allows absorbing a substantial fraction of solar spectrum. Iron oxide (α -Fe₂O₃) hematite films were prepared by advanced pulsed plasma deposition method of High Power Impulse Magnetron Sputtering (HiPIMS). Tungsten trioxide films were prepared by sedimentation of WO₃ particles. The films were judged on the basis of physical properties such as crystalline structure, optical absorption, surface topography and electrical behavior. The functional properties were investigated under simulated photoelectrochemical (PEC) water splitting conditions. As deposited WO₃ films have rather small photocurrents. Higher annealing temperature results in better adhesion of particles and increase in photocurrent. Optimum annealing temperature is 450-500 °C, increasing of the annealing temperature above 500 °C caused the formation of undesirable crystal phases and significant decrease in photocurrent. Despite revealed hematite phase of as-deposited films, these were almost photoelectrochemically inactive. The annealing in air at 650 °C significantly improved photoefficiency which can be explained by the diffusion of tin from the FTO substrate into hematite resulting in the extrinsic doping of hematite improving its electronic properties.

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Catalytic oxidation of volatile organic compounds over ceria-zirconia supported noble metal catalysts

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Abstract

Catalytic oxidation is a green and efficient way to handle man-made emissions of volatile organic compounds (VOC), which represent serious environmental issue. Despite high purchasing costs, supported noble metal catalysts are favored over metal oxides due to their high activity and selectivity, excellent stability and superior resistance against poisoning. In the present work, ceria-zirconia mixed oxide was employed as a support for gold and platinum catalysts that were characterized and tested in the gas-phase oxidation of model VOCs to investigate the influence of noble metal loading and type on the catalytic performance and selectivity of the catalysts. In the oxidation of dichloromethane, the noble metal catalysts showed lower catalytic performance than the parent $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ due to lower amount of acid sites that act as chemisorption sites for chlorinated compounds. However, platinum catalysts exhibited significantly enhanced selectivity to CO_2 . In contrast, the catalytic performance in chlorobenzene oxidation was increasing with increasing noble metal content. The positive effect of noble metal addition was ascribed to the oxidation of chlorine species, which block the active sites, by noble metals. In ethanol oxidation, the catalytic performance increased linearly with increasing Pt content and the influence of Pt loading on the mechanism of ethanol oxidation was revealed, while the introduction of gold had only a minor effect. Finally in toluene oxidation, only platinum catalysts with 0.35 wt. % and higher loading exhibited better catalytic performance than the pure support.

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Photocatalytic mitigation of greenhouse gases on cerium doped TiO₂ prepared by using pressurized and supercritical fluids

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Abstract

Ce/TiO₂ photocatalysts with various Ce loadings were prepared using the sol-gel process controlled within the reverse micelles and processing by pressurized and supercritical water and methanol. Since microstructure is responsible for the photocatalytic performance of materials, textural, micro/structural and optical properties of prepared photocatalysts were characterized by N₂ physisorption, powder X-ray diffraction, transmission electron microscopy combined with electron diffraction, DRS UV-vis spectroscopy in order to correlate them with their catalytic performance in CO₂ photocatalytic reduction and/or photocatalytic decomposition of nitrogen compounds (*i.e.* N₂O, NH₃).

Acknowledgement

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Effect of ZnO preparation method on the photocatalytic decomposition of ammonia in aqueous suspensions

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Abstract

Ammonia direct photocatalytic decomposition is a promising process for production of carbon monoxide-free hydrogen. The products of NH₃ decomposition are N₂ and H₂, which are quite benign to environments. ZnO nanoparticles were prepared by precipitation reactions of zinc acetate and sodium hydroxide at room temperatures without stabilizing agents at different ratios of zinc and hydroxide ions and consequent calcination at 350-700° C. The precipitation was also performed under UV irradiations forming the smallest nanoparticles. The prepared nanoparticles were characterized by XRD, FTIR, Raman, UV-Vis, luminescence spectroscopy, electron microscopy and tested for NH₃ photocatalytic decomposition under the 254 nm UV light. The correlation between preparation method, physical-chemical properties and photocatalytic activity is discussed.

Acknowledgement

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TiO₂-CeO₂ prepared by using pressurized and supercritical fluids; Effect of processing parameters on micro/structural and morphological properties

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Abstract

Nanostructured TiO₂-CeO₂ belongs among materials under keen research interest because of its visible light induced activity and promoting effect of noble metals as a catalyst support. The utilization of pressurized and supercritical fluids for the preparation of nanostructured materials introduces a new scientific challenge concerning the effect of various processing conditions (*i.e.* temperature, pressure *etc.*) on the micro/structural and morphological properties since the crystallization takes place under different thermodynamic conditions than during common thermal treatment. In a consequence the nanostructured material possessing different/improved electrochemical, optical and photo/catalytic properties can be obtained. The preparation of TiO₂-CeO₂ (with various Ce concentrations) by using the sol-gel technique and/or hydrolysis and processing by pressurized water and pressurized/supercritical methanol or carbon dioxide was studied in order to reveal the relationship between individual processing conditions at elevated pressure and TiO₂-CeO₂ microstructure and purity.

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Physico-chemical properties and catalytic behaviour in propane ODH of mesoporous vanadosilicate prepared by Pluronic P123 templating route

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Abstract

Various silica based vanadium catalysts attract big attention for their activity in oxidative dehydrogenation (ODH) of light alkanes. Recently, we prepared, by solvothermal synthesis in the presence of Pluronic P123 as a template, vanadosilicate catalyst exhibiting high volume of mesopores and superior catalytic activity in ODH of n-butane with productivity of butenes $1.92 \text{ kg}_{\text{prod}} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$. It ranks this catalyst among the best material investigated so far in this reaction. In this contribution, we focus on catalytic behaviour of mentioned material in ODH of propane and its comparison with common catalysts prepared by impregnation of vanadium precursor into mesoporous SBA-15 silica.

All catalysts were characterized by XRF, N₂-BET, H₂-TPR, Raman and UV-Vis spectroscopies. The catalytic behaviour was investigated in ODH of propane at 540 °C in reaction mixture consisting of 2.5 mol. % of O₂ and 5 mol. % of propane in helium. Characterization results showed that solvothermal synthesis led to higher population of tetrahedral oxo-vanadium monomeric complexes in comparison with impregnation. Difference in catalytic behaviour was not so dramatic like in ODH of n-butane indicating significant differences in active sites for both mentioned reactions.

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Optimization of Cs content in Co-Mn-Al mixed oxide as catalyst for N₂O decomposition

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Abstract

The series of Co-Mn-Al mixed oxide catalysts with different amount of Cs (0.5–4.6 wt.%) was prepared by calcination of Co-Mn-Al hydrotalcite (Co:Mn:Al = 4:1:1) and followed by impregnation by cesium salt (CsNO₃, Cs₂CO₃) using pore filling method. Chemical analysis, XRD, N₂ sorption, TPR-H₂, TPD-CO₂ and TPD-NH₃ were used to characterize the catalysts. All prepared catalysts were tested for N₂O catalytic decomposition in inert gas and in the presence of oxygen, water vapor and nitric oxide. The influence of Cs salts used for catalyst preparation, cesium amount and calcination temperature on catalysts activity and stability were studied. The catalytic activity increases with increasing amount of cesium promoter. The catalysts containing ca. 3.2 wt.% Cs was the most active one under the conditions simulating the composition of the waste gas (N₂O, O₂, H₂O) upstream the SCR NO_x unit in a nitric acid plant.

Acknowledgement

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Interdigital electrochemical cells fabricated by inkjet printing

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Abstract

Planar, interdigitated photoelectrochemical cells were made in a fully additive way by ink jet printing. The base electrode system of variable geometry and finger density was fabricated by printing commercial gold resinate ink onto alumina substrates of 26x76 mm size and firing at 800 °C. Resulting gold electrodes were overprinted by titanium dioxide of different origin (compact and mesoporous sol-gel process, nanocrystalline dispersion), various thickness and various curing conditions. The interdigital geometry ensured that the photoelectrochemical response of the printed cells was not suffering from iR drop down to low electrolyte ionic strengths. The best performing electrode designs were then scaled-up and 10x10 cm prototype cells were fabricated. The photoelectro-catalytic degradation of an aqueous solution of terephthalic acid by UVA illumination and electric bias of 1 V was demonstrated by build-up of fluorescence of an OH-substituted molecule.

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Effect of Co dopant addition in Mo/ZSM-5 catalyst for methane dehydro-aromatization

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Abstract

Methane dehydro-aromatization (MDA) represents a reaction with high application potential and could provide a crucial process for methane conversion into valuable products and the way for compensation of the declining oil resources. The mostly studied for this reaction are the Mo-zeolite catalysts and their various modifications. The addition of a Co was identified as having a positive impact on MDA when combined with standard molybdenum based catalyst. In the previous studies (Y. Xu, Applied Catalysis A: General, **2011**, 409-410, 193) the co-impregnation method was used for catalyst preparation.

In the present contribution the variation of the sequence of Mo and Co addition was studied in detail and evaluated its effect on the methane conversion. The selectivity to aromatics and other byproducts is discussed, along with data obtained by the elementary analysis of coke on spent catalysts.

Strong dependence of the order of Mo and Co addition was observed on benzene production as well as on the coke formation, directly responsible for the catalyst deactivation.

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Ni-alumina catalysts in oxidative dehydrogenation of ethane and enhanced catalytic behavior after cerium addition

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Abstract

Nickel based catalysts are widely used in steam reforming of methane producing synthesis gas, hydrogenation and hydrocracking. In last decade are Ni-based catalysts studied in oxidative dehydrogenation of light alkanes such as ethane and propane. This is alternative way of olefin production to the fluid catalytic cracking, steam cracking and pyrolysis.

In oxidative dehydrogenation of light alkanes was published that promoters like Nb, W or Ce can enhance the catalytic activity of Ni-based catalysts. Most of these works deal with mixed oxides Me-Ni-O (Me=Nb, W, Ce etc.).

The current work deals with oxidative dehydrogenation of ethane over Ni-catalysts promoted by Ce. The catalysts were prepared by impregnation of commercial alumina or Al-Ce-O mixed oxides prepared by co-precipitation and sol-gel method. For characterization was used XRD, H₂-TPR, DR UV-Vis spectroscopy. The reaction was take place in quartz flow-through reactor. The catalyst was diluted with SiC. Composition of reaction feed was 7.5 % C₂H₆, 2.5 % O₂ and 90 % He, with total flow 100 ml.min⁻¹.

Ce addition affects the structure and relative population of Ni-species in Ni-alumina catalysts. Cerium addition enhances the catalytic activity in ODH of ethane. The impregnation order between Ni and Ce significantly affects the structure of Ni-species and catalytic behavior respectively.

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Photocatalytic degradation of acetone and methanol on TiO₂

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Abstract

Volatile organic compounds are necessarily used in many industrial processes, which involve their emission into the environment in the form of waste gas. Photocatalysis in gaseous phase is a method of purification of exhaust gases without producing further by-products. Degradation of different compounds naturally differs, thus it is important to study the influence of operational parameters in the cases of individual compounds. This paper compares the degradation of vapors of acetone and methanol.

For this study, we use 90 cm long tubular reactor with TiO₂ photocatalyst irradiated externally by eight either UV-A or UV-C 30W lamps. The feed air stream is prepared by mixing air and small amount of liquid pollutant completely evaporated. The inlet and outlet analysis is done by gas chromatograph.

Influence of the irradiation wavelength was the main studied parameter. We used equal volumetric feed of liquid in the air stream for both pollutants, which resulted in the concentration of acetone about 275 ppm and of methanol about 500 ppm. In separate experiments, using UV-A lamp, the conversion of acetone was 29 %, while the for methanol was 72 %; methanol is degraded easily than acetone. This might be explained by the different molecular structure; decomposition of larger C₃ acetone molecule requires more complex bond breakage in the comparison to smaller C₁ methanol molecule. For UV-C lamps the conversion of acetone significantly increased (to 60 %), while the one of methanol increased only slightly (to 80 %). The increase of the acetone conversion is not only due to the light energy (change from 365 to 254 nm) but also due to acetone adsorption at 256 nm resulting in significant contribution of direct photolysis.

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Alternative way of aromatics preparation by methane dehydroaromatization

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Abstract

It is estimated that crude oil reserves will be sufficient for only a few decades. Therefore, it is now necessary to look for alternative sources for the production of petroleum hydrocarbons. The methane dehydroaromatization reaction is an alternative for producing aromatics from another source than crude oil. This reaction runs at high temperatures (700-900°C), at atmospheric pressure, in the presence of a catalyst and without the presence of air. Many catalytic systems were tested in this process, and among all the best catalytic system is the Mo/ZSM-5. The main products in this process are benzene, toluene, naphthalene and hydrogen. This process is in the phase of laboratory research. The researchers are looking for a suitable catalytic system to increase the methane conversion.

Our aim was to prepare catalysts with different methods of molybdenum loading, and test these catalysts in methane dehydroaromatization. The catalysts were characterized with standard methods (n-hexane conversion, FTIR, TPDA, XRD, surface characteristics). XRD measurements confirmed the presence of crystalline MoO₃ on some samples. The acidity of the parent zeolite was 1.05 mmol/g. The acidities of the catalyst samples decreased to 0.8-0.9 mmol/g after molybdenum loading. The highest conversion was reached in 60th minute of TOS, above 14%.

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One pot synthesis of Au and Pd catalysts supported onto functionalized polymeric resin for selective oxidation of glycerol to carboxylic acids

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Abstract

Glycerol from biomass is a potential starting material for various high value fine chemicals where the carboxylic acids, such as glyceric acid and tartronic acid play a significant role. The application of heterogeneous catalysts and molecular oxygen in selective oxidation of glycerol offers a green alternative to traditional toxic chemical oxidants. The oxidation reaction of glycerol is catalyzed by noble metals mostly supported on active carbon. The selectivity depends not only the type of active phase, but it is influenced by numerous parameters, such as the metal particle size, the pore size of the support and the pH of the reaction medium. Usually the catalysts are prepared by complex methods and using additional compounds to ensure the expected metal particle size. In the present work one-pot synthesis of Au and Pd nanoparticles supported onto commercial anion-exchange resin was studied. The catalytic performance for the selective oxidation of glycerol with molecular oxygen in aqueous solution at pH 11 and atmospheric pressure was compared. Between Au and Pd particles synergism was observed. Activity and selectivity of the catalysts influenced the amount of the metals loaded on the support. The possibility of the catalysts recycling is discussed.

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Direct conversion of cellulose to ethylene glycol over tungsten phosphide catalysts

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Abstract

One of the most attractive routes for cellulose utilization is its direct conversion to ethylene glycol (EG). It is an important intermediate used for producing many chemical compounds, such as polyester fibers, resins and polyethylene terephthalate. At present time, in the petrochemical industry is EG produced from ethylene and via corresponding oxide as chemical intermediate. Due to the increasing consumption of EG, the direct conversion of cellulose opens new possibilities for reducing the oil dependency.

The tungsten phosphide catalysts supported on active carbon were prepared and evaluated in hydrogenolysis of cellulose to ethylene glycol. The reaction was carried out in a batch reactor at 200 °C and 4 MPa of hydrogen pressure. A maximum yield of ethylene glycol about 42 mol. % was achieved over WP/AC catalyst with 30-40 wt. % loading of active WP phase. The addition of 2 wt. % nickel in low concentrations significantly increased the formation of ethylene glycol to about 61 mol. % with simultaneous decrease of butane diols formation (from about 35 to 15 mol.%).

Triglycerides into motor fuels: the role of zeolite ZSM-5

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Abstract

Today's situation of fossil energy resources enhances the research in the field of alternative fuels production mainly from renewable materials. Thermochemical upgrading of vegetable oils under conditions of catalytic cracking could effectively serve this purpose. As vegetable oils consist mostly of triglycerides, a forming of water and organic oxygenates in the liquid products and CO and CO₂ in the gaseous products is expected to occur. Thus the catalytic system has to be resistant towards the deactivating effect of steam and simultaneously to be able to convert undesired organic oxygenates into hydrocarbons. In means of the former condition we decided for the fluid catalytic cracking process, as the FCC catalyst is naturally steam-resistant. To meet the latter condition we used the hydrothermally stabilized ZSM-5 additive to the FCC catalyst to maximize the conversion of oxygenated organics. The catalysts were tested under Micro-activity test conditions. Rapeseed oil was used as feed. The main monitored factors were the quality and quantity of the gasoline fraction and the amount of unconverted organic oxygenates, for which gas chromatography-mass spectrometry was used. Mainly phenol, alkyl-substituted phenols, carboxylic acids and a small amount of acetone were identified in the liquid product.

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Alkylation of benzene with 1-alkenes over chemical and thermal dealuminated zeolite Y

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Abstract

The alkylations of aromatic hydrocarbons with different 1-alkenes or alcohols are applied on a large scale in the chemical industry. As alkylation catalysts mainly Friedel-Crafts type catalysts as Brønsted and Lewis acids are frequently used (H_2SO_4 , HCl , AlCl_3 , BF_3 ...). Because of problems with corrosion and high requirements on feed drying there is an effort to replace FC-catalysts with solid acids. Zeolit Y appears a suitable catalyst for the alkylation of aromatics with 1-alkenes in the liquid phase. Zeolite Y in NH_4 - and H-form can not be regenerated and therefore it is necessary to treat it. Chemical ($(\text{NH}_4)_2\text{SiF}_6$, H-EDTA) and thermal dealumination (deep bed treatment) is suitable method for improvement of physico-chemical and catalytic stability.

We prepared chemical dealuminated zeolites Y with $(\text{NH}_4)_2\text{SiF}_6$ and H-EDTA and thermal dealuminated zeolites Y in deep bed at the temperature of 560°C with followed by extraction of extra-framework aluminum with hydrochloric acid. There prepared zeolites Y were characterized by X-ray diffraction, temperature programmed desorption of ammonia, FTIR adsorption of pyridine and surface characteristics were measured by adsorption of nitrogen. Alkylation was carried out in a batch mixed reactor at 120°C . Results showed that different degrees of dealumination and different secondary mesoporous systems were created after diverse used treatment. The alkylation of benzene with 1-alkenes confirmed the improvement of catalytic properties of treated zeolites Y. The highest conversion of 1-alkenes showed the sample prepared in deep bed treatment with followed by extraction of extra-framework aluminum with hydrochloric acid.

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Copper and iron pyrophosphate catalysts for selective oxidation of biogas to formaldehyde

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Abstract

Biogas is a product of anaerobic biodegradation of biomass and its main components are methane (35-65%) and carbon dioxide (15-50%). Biogas can be thus utilized as an alternative to methane derived from natural gas. Due to high stability of the C-H bond in the methane molecule, the activation of methane requires high temperatures or an efficient catalyst. Since the desired products, formaldehyde or methanol, are readily decomposed at higher temperatures, the corresponding oxidation reaction is catalyzed by various metal oxides with high dispersion supported on macroporous silica. The present work is focused on the selective oxidation of biogas over bulk Cu-Fe-pyrophosphate catalysts. The catalysts were prepared by sol-gel method in the presence of structure directing agent and calcined at different temperatures. Their catalytic properties for selective oxidation of biogas to formaldehyde in the temperature range of 400-630°C and at atmospheric pressure were studied. Biogas consisting of 60 vol.% and 40 vol.% of CH₄ and CO₂, respectively was oxidized by nitrous oxide as oxidizing agent and the results were compared with the oxidation of pure methane. The highest yield of desired product, formaldehyde, in the temperature range of 550 – 575°C was obtained. The possibility of using CO₂ as potential oxidizing agent of methane without presence of N₂O or other oxidizing agent was also verified. The activity and selectivity of the catalyst using biogas or methane was found to be stable during the studied more than 25 h of time on stream.

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The photocatalytic activity of metal-doped zinc oxides (An EPR study)

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Abstract

The binary metal oxides as interface materials play an essential role in the design of efficient and stable bulk heterojunction (BHJ) solar cells. Recently, titanium oxide or zinc oxide thin layers have been successfully applied as an electron/hole transport and an electron/hole extraction layer in the inverted BHJ organic solar cells. Nowadays, the research is mainly oriented on the synthesis and characterization of ZnO or TiO₂ nanostructures in order to improve the function of these layers. The ZnO samples undoped and doped with nickel (Ni²⁺), cobalt (Co²⁺) and aluminum (Al³⁺) ions prepared by classical sol-gel method and non-hydrolytic sol-gel (solvothermal) method were studied. The work was oriented on the testing and assessment of ZnO's photoactivity upon UVA excitation. The majority of photochemical/photocatalytical processes is coupled with the generation of paramagnetic species, therefore, the electron paramagnetic resonance (EPR) spectroscopy was applied. Due to the short lifetime of the generated intermediates their direct evidence is not possible and various indirect approaches, such as EPR spin trapping technique using various spin traps, elimination of semi-stable free radicals or oxidation of hindered amines, were necessary for their monitoring.

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Photoinduced processes on titanium dioxide investigated by EPR spectroscopy

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Abstract

Nanocrystalline titanium dioxide polymorphs (anatase, rutile, brookite) are intensively studied due to their unique properties utilized in catalysis, pigment and cosmetic industries, environmental technologies for water and air purification and in the production of glass and ceramic materials possessing self-cleaning ability. The charge carriers (electrons and holes) produced upon photoexcitation of semiconducting TiO_2 initiate redox reactions often coupled with the generation of paramagnetic intermediates. For example the efficient elimination of organic pollutants in aerated aqueous systems using powdered or immobilized TiO_2 photocatalysts is based on the photoinduced formation of reactive oxygen species, especially hydroxyl radicals. Consequently, EPR spectroscopy represents a useful tool for the characterization of TiO_2 nanomaterials providing the information on the structure, origin and concentration of the photogenerated paramagnetic intermediates. The EPR spin trapping technique employing a variety of spin trapping agents was used for the monitoring of hydroxyl radicals upon TiO_2 photoexcitation in aqueous suspensions, and this technique was also successfully applied for radicals detection in irradiated titania suspended in organic solvents. Moreover, in non-aqueous media photogenerated electrons may react with suitable electron acceptors (*e.g.* nitroaromatic compounds) producing the corresponding radical anions evidenced by *in situ* EPR spectroscopy. Our contribution shortly summarizes previous and recent studies on the paramagnetic species detected in the irradiated TiO_2 systems under different experimental conditions.

Acknowledgement

This work was supported by the Scientific Grant Agency of the Slovak Republic (Project VEGA 1/0289/12).

Effect of the exposed {001} crystal facets in anatase nanostructures on the photocatalytic performance (an EPR study)

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Abstract

Photoinduced processes undergoing upon the excitation of novel TiO₂ photocatalysts were studied *in situ* by electron paramagnetic resonance (EPR) spectroscopy. Since these reactions are closely linked with the generation of reactive intermediates of different stability, for their monitoring various techniques of cw-EPR spectroscopy and EPR measurements at low temperatures were applied. The obtained information on the character, concentration and origin of the reactive species generated in the irradiated TiO₂ suspensions in various solvents were utilized to assess the photocatalytic activity of individual nanostructures. The studied samples, synthesized in accord with the latest findings linking the photoactivity directly with the crystalline structure, represented Mg(II)-doped/undoped anatase nanocrystals with exposed {001} crystal facets. The well-established EPR indirect methods for the monitoring of reactive radical/nonradical intermediates in the TiO₂ suspensions were applied and the relevance of so obtained results was considered in the scope of their application for the photoactivity assessment. The low temperature experiments (down to 100 K) provided a direct evidence of the paramagnetic centers generated upon the photoexcitation of studied TiO₂ nanopowders.

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Phase separation in metal oxide nanoparticle systems

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Abstract

Combustion synthesis of metal oxide particles can provide nonequilibrium mixtures thereof. After combustion of Ba, Zn or Fe in the MgO formation flame and immediate quenching related particle systems are characterized by a statistical distribution of the components. Differences in ionic radii or valence states of the admixed cations drive their annealing induced segregation into the particle surface. Related effects were utilized to generate composite surface structures with altered chemical and optical properties. On Ba-Mg-O particle systems electron microscopy reveal MgO-based support particles with hemispherical BaO phases.[1] Structural and energetic properties of BaO units dissolved inside the MgO host and adsorbed on MgO surface were investigated by DFT calculations. Ab initio thermodynamics revealed that the segregate shape results from the growth process and become stabilized by surface hydroxylation. As another example, Zn-Mg-O particles were synthesized in the range from solid solutions of Zn ions in MgO to phase separated particle mixtures.[1,2] We demonstrate for composite particles, that the admixed ZnO produces bulk related PL emission and suppresses MgO specific surface excitons. Obtained insights are relevant for composite metal oxide nanoparticles as catalyst materials where the impact of dynamical changes in the interface composition plays a critical role.

[1] Sternig et al. J. Phys. Chem. C 115 (2011) 15853.

[2] Zhang et al. ACS Appl. Mater. & Interfaces 4 (2012) 2490.

Cobalt Oxide Model Catalyst as Alternative to Noble Metal Catalysts

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Abstract

Cobalt oxide has recently turned out to be a novel, highly active heterogeneous catalyst for many industrial important reactions. Most important, cobalt oxide-based catalysts hold an unique potential for replacing or reducing the demand for critical materials (noble metals and rare earth oxides). However the origin of the high cobalt oxide activity in catalysis is still not cleared.

We have chosen a thin cobalt oxide films with a defined structure as model catalysts for low temperature CO oxidation. The cobalt oxide film was formed on the surface of an Ir(100) single crystal by physical vapor deposition (PVD) in O₂ flow with a subsequent post-oxidation step. With this routine a 6 ML thick Co₃O₄(111) and CoO(111) film was prepared. The characterization of films has been performed by low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS).

Further we investigated the state of active component and interaction of CO, CO₂ and gas mixture (CO+O₂) with different surfaces of cobalt oxide by XPS, polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) and thermal programmed desorption (TPD) in the temperature range 200 K – 470 K and in the pressure from UHV to 100 mbar.

It has been shown that CO does adsorb on cobalt oxide films at used temperatures and pressure ranges. Using XPS and PM-IRAS it has been shown that for both Co₃O₄(111) and CoO(111), depending on the conditions of CO adsorption, we obtained appearance of two different carbon-contained species which could be identified as carbonates and elementary carbon. Furthermore in case of Co₃O₄(111) film CO adsorption leads to partial reduction of cobalt oxide even at UHV conditions (pressure of CO in gas phase 1×10^{-6} mbar) and room temperature. The thermal stability of carbonates and elementary carbon formed during the CO adsorption on Co₃O₄(111) film was investigated by thermo desorption spectroscopy (TDS). It has been shown that both of it desorbed from the surface at 520 K -700 K as CO₂, at the same time Co₃O₄(111) film has been reduced to CoO(111).

Also it was shown that it is possible to recover the film (initial state of composition and structure) after CO adsorption and desorption experiments by oxidation treatment at 550 K and a subsequent annealing at UHV to 670 K.

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In situ studies of CO oxidation and preferential CO oxidation on Co₃O₄ nanostructured catalysts

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Abstract

In spite of the intensive studies of CO oxidation and preferential CO oxidation (PROX) over cobalt oxide, the nature of the active sites as well as the reaction mechanisms are still under debate. Open questions and contradicting results concern, for instance, the role of Co²⁺/Co³⁺, different oxygen species, oxygen vacancies, formation of carbonates, influence of pretreatment, moisture in the feed and the cause of catalysts deactivation. This is because the current understanding of these reaction systems is mostly based on ex situ analyses of the catalysts and kinetic experiments. Thus, an in depth investigation of Co₃O₄ by employing in situ surface sensitive techniques is required for elucidating the nature of active sites and the reaction mechanisms.

In this contribution we will focus on studying the nature of active sites of cobalt oxide catalysts and the reaction pathways for CO oxidation and PROX. Furthermore, the influence of the catalysts shapes, e.g. nanoparticles and nanorods, as well as pretreatment conditions on the CO oxidation catalytic activity and selectivity in PROX are investigated. Our in situ IR spectroscopy results clearly show that CO does not adsorb on Co³⁺ and Co²⁺ ions of Co₃O₄ catalysts but forms surface carbonate species (bidentate, and monodentate), while upon CO₂ introduction only a small amount of weakly bonded bicarbonate is formed. Different surface carbonate species were also observed during CO oxidation (CO/O₂=1/2) and during the PROX (CO/O₂/H₂=1/1/50) in the temperature region of the predominant oxidation of CO to CO₂. Thus, we propose that either bidentate or monodentate carbonate species are potential reaction intermediates. In catalytic tests it was found that Co₃O₄ nanorods are more active than nanoparticles in CO oxidation as well as in PROX and that reduction pretreatment lowers the catalytic activity for both nanoshapes compared to oxidation pretreatment.

Characterization of methanization and methane reforming catalysts: Ni-STF and Ni-LSF

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Abstract

Perovskites are currently the most popular material for SOFC cathodes. Our approach is to use them as anode materials. Since perovskites are mixed ionic and electronic conductors (MIECs), both oxygen ions and electrons can be transported quite effectively to and from the triple phase boundary, where the following reaction takes place:



Two different perovskites, LSF ($\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-d}$) and STF ($\text{SrTi}_{0.7}\text{Fe}_{0.3}\text{O}_{3-d}$), were impregnated with nickel and investigated concerning their methanation and methane reforming activity. After a defined pre-treatment, the reaction mixture (CO_2 , H_2 and H_2O for methanation and CH_4 and H_2O for the methane reforming reaction) was dosed and the reactor was heated up to 600 °C and the gas phase composition continuously monitored by mass spectrometry and gas chromatography - mass spectrometry.

For Ni-STF the methanation reaction starts at 250 °C. The methane maximum pressure is reached at 400 °C. At higher temperatures methane reforming yields increasing amounts of carbon monoxide. Also for Ni-LSF, methanation activity can be monitored, starting at 300 °C. At 370 °C methanation competes with the inverse water- gas shift reaction and carbon monoxide is formed. Above 550 °C the formed methane is again reformed.

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Reactivity difference of Al and Zr ALD/CVD precursors: nanostructure drives the chemistry

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Abstract

To prepare an active “inverse” methanol-reforming Zr^0 -(pre)-catalyst on Pd- and Cu-metal substrates, a novel ALD/CVD approach was compared to results of previous experiments using a self-developed sputter device. The latter, sputter-based experimental series already showed that H_2O activation sites exist in the $\text{Zr}(\text{ox})$ -Cu system, combining Zr redox activity with water activation ($\text{ZrO}_2 \leftrightarrow \text{ZrO}_{2-x}$). The ALD/CVD technique using organometallic Zr precursors was originally used to prepare thin insulating layers of ZrO_2 , aiming to scale down microelectronic devices. This ALD/CVD system was now adopted for inverse model catalyst synthesis, however, different kinds of interaction between precursor, Zr and catalytically active substrate have been observed for different metals.

ALD/CVD of Zirconium-t-butoxide (ZTB) was investigated on Cu(111) and Pd(111) single crystals using XPS, STM, HREELS and LEED. The aim was to prepare a metallic Zr (sub-) monolayer film on a metal substrate as an inverse pre-catalyst to maximize potential bi-functional sites induced by ZrO_x segregation under reaction conditions. Alternatively, a ZrO_2/ZrOH layer with a high number of active interface sites can already be formed via organic precursor hydrolysis and/or oxidation. The Zr results were compared with Al on Pd(111), using Tri-methyl-aluminum (TMA) as a precursor. Differences in particle topography/size result in significant differences in redox activity of Al and Zr.

Temperatures between 300°C and 550°C are required for Zr^0 deposition via decomposition of the volatile ZTB on Pd(111). The organic moieties of the precursor can easily be removed by heating in vacuum, leading to subnanometer Zr^0 clusters of a few atoms. These clusters behave very different as bulk Zr^0 with respect to redoxactivity. The subnano-Zr can be oxidized or hydroxylated reversibly and, by annealing in vacuum at 400°C, it can be very easily reduced to Zr^0 again. This unusual behavior was not observed for Al, according to STM, because no subnano Al-clusters but rather big particles were formed on Pd(111).

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***In situ* studies on the synergetic effect between Pd species and Co₃O₄ and Fe₂O₃ in CO oxidation**

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Abstract

Recently it has been reported that the introduction of noble metals to transition metal oxides (e.g. Co₃O₄, NiO, Mn₂O₃, Fe₂O₃) largely enhances their catalytic activity in CO oxidation. This enhancement is often attributed to the strong metal-support interactions. However, the nature of these interactions is still under debate. Therefore, the aim of our work was to investigate: 1) the mutual interaction between the metal oxide (Co₃O₄ or γ -Fe₂O₃) and the noble metal Pd; 2) the oxidation states of Pd and Co or Fe and the correlation with the activity of Pd supported on Co₃O₄ or γ -Fe₂O₃ catalysts in CO oxidation.

We prepared 2 wt% Pd/Co₃O₄ and Pd/Fe₂O₃ catalysts by wet impregnation of commercial Co₃O₄ and γ -Fe₂O₃. The addition of Pd to γ -Fe₂O₃ strongly enhanced the catalytic activity, for both, the pre-oxidized as well as H₂-reduced (100 °C and 300 °C) Pd/Fe₂O₃ catalysts compared to pure γ -Fe₂O₃. Adding Pd to Co₃O₄ also increased the activity after oxidative pretreatment compared to pure Co₃O₄. However, the catalytic activity was decreased for the Pd/Co₃O₄ catalyst reduced in H₂ at 100 °C. *In situ* FTIR showed that on oxidized Pd/Co₃O₄, carbonates were formed in presence of the reaction mixture (CO/O₂=1/2), and surprisingly, no CO adsorption bands on Pd were found. Therefore we assume that PdO is the stable phase under these conditions and carbonates are possible reaction intermediates. In contrast, the oxidized Pd/Fe₂O₃, showed bands of CO adsorbed on Pd (linear and bridged) increasing over time after introduction of the reaction mixture at room temperature due to the reduction of PdO to Pd. Thus, strongly different behavior was observed for Pd supported on Co₃O₄ compared to Pd on γ -Fe₂O₃.

Transient *in situ* doping of TiO₂ nanostructures: Implications for photocatalysis

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Abstract

Semiconductor oxides constitute a versatile class of materials for electronic, optical, environmental and energy applications [1]. These materials show not only suitable intrinsic properties, but are furthermore susceptible to systematic alterations of their characteristics by bulk or surface modification. Some semiconductor properties, such as the doping degree, turn out to depend not only on material synthesis and processing, but may furthermore significantly change *in situ* (i.e. during operation). It will be shown that such a dynamic change can have important implications for material performance.

In this contribution the photoinduced *in situ* doping of mesoporous anatase TiO₂ films in aqueous media will be highlighted. This process is connected to the accumulation of photogenerated electrons in the semiconductor compensated by counter-ion (H⁺) uptake from solution. Such a transient charge accumulation is shown to significantly improve the activity of the TiO₂ films in photooxidation reactions as tracked by open circuit potential or photocurrent measurements, respectively. Importantly, it was found that the photocatalytic performance enhancement does not depend on the type of perturbation, if, alternatively, an external bias voltage or band gap excitation at open circuit were used to set the Fermi level position in the semiconductor during doping [2,3]. The influence of particle morphology on doping persistence and implications for photocatalysis will be discussed.

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Application of heterogenized metal complexes in hydrogenation reactions: a comparison of hydrogenations and CTH reactions

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Abstract

The preference of heterogeneous catalysts over the homogeneous ones is well known in the fine chemicals industry. However, considering activity and selectivity the metal complexes as homogeneous catalysts are usually suppressed by the heterogeneous counter-parts. Consequently an increasing demand has developed toward the application of heterogenized metal complexes as catalysts which can combine the advantages of both catalysts types. In the production of fine chemicals the selectivity is probably the most important property. Chemoselectivity, regioselectivity and enantioselectivity play very important role in the synthesis of fine chemicals. Several examples of hydrogenations were studied on heterogenized metal complexes and the selectivity issue will be emphasized in this contribution. Catalytic transfer hydrogenations (CTH) will be also discussed as alternative methods to the classical hydrogenation processes.

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A new way to obtain CO-tolerant Pt/Ti_xW_(1-x)O₂-C anode electro-catalysts. Application for hydrogen fueled PEM fuel cells

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Abstract

A key requirement for widespread implementation of fuel cells is the development of advanced anode electrocatalysts with reduced Pt content, simultaneously increased metal dispersion, high stability and CO tolerance. As novel anode electrocatalysts, Ti_xW_(1-x)O₂ mixed oxide and activated carbon (C) composites were prepared by using three different sol-gel-based multistep synthesis routes. It has been demonstrated in our earlier study that preliminary formation of the rutile phase in the presence of C at room temperature (RT) before any high temperature treatment is prerequisite for the complete W incorporation into the rutile lattice upon reductive treatment at 650°C. Upon using of this synthesis route high reproducibility in the formation of rutile phase with high crystallinity and exclusive W incorporation has been achieved. In this contribution our results obtained in development of Ti_xW_(1-x)O₂-C composites with x= 0.6, 0.7, 0.8 and Ti_xW_(1-x)O₂/C= 50:50 ratio will be shown. The influence of (i) the type and amount of acid used upon the Ti-sol formation, (ii) the duration of the Ti-sol aging before the addition of C, and (iii) the prolongation of RT aging before the addition of ammonium metatungstate on the rutile/anatase ratio will be discussed. Details on the characterization of Ti_xW_(1-x)O₂-C composites by XPS, TEM and EDS techniques will be demonstrated. Finally, electrochemical results revealing improved CO tolerance of the 40 wt% Pt/Ti_{0.7}W_{0.3}O₂-C anode electrocatalysts and high activity in hydrogen electrooxidation will be presented.

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Water-soluble metalloporphyrins as photocatalysts for utilization of visible light

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Abstract

Due their special spectral, coordination and photoredox features, metalloporphyrins can be used in various photocatalytic procedures, e.g., for utilization of solar radiation.

In the presence of suitable electron donor and acceptor, kinetically inert (in-plane) cationic Mn(III), Co(III), and Ni(II) porphyrins proved to be efficient photocatalysts transferring electrons between these two ground-state reactants. These photocatalytic systems can also be utilized for hydrogen generation in aqueous systems. While Mn(II) and Co(II) centers formed in the primary step need also photoexcitation for the transfer of electron to the ground-state acceptor, the photogenerated reactive Ni(I) intermediate can thermally undergo this redox reaction.

Lanthanide(III) porphyrins are of typical kinetically labile (out-of-plane) complexes, the photoinduced behavior of which can be tuned by the size of the metal center. These complexes may also serve as catalysts in water-splitting by visible light.

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New theory of H₂S inhibiting effects in HDS process

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Abstract

It is generally accepted, sulphur vacancies are active sites of catalytic hydrodesulfurization HDS process on the surface of transition metal sulfides (TMS) catalysts and H₂S inhibits hydrodesulfurization (HDS). Indeed H₂S is competitively adsorbed on the active sites that decreases the total number of available CUS sites, and convert CUS into –SH, although Vogelaar et al. pointed out the one of the reason for deactivation of catalysts during thiophene HDS is the loss of sulfur from the active phase during HDS mechanism. It follows that too much sulfur vacancy not increases the HDS activity of the catalysts. There is a contradiction between above facts. If we want to solve this contradiction we have to know more about the active sites during HDS process.

Massoth et al. observed a linear correlation ($R^2 = 0,90$) between the total sulfur exchange capacity and thiophene hydrodesulfurization (HDS) activity of different alumina-supported molybdenum-and tungsten-oxide catalysts. A number of studies have described some kind of correlation between on supported sulfide catalysts and hydrodesulfurization (HDS) activity. This result shows there can be any correlation between exchangeable sulfur species and active sites. In present work we investigated is there any correlation in case new generation catalysts, and how active sites behave in reaction condition.

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Synthesis and catalytic application of palladium-graphite oxide nanocomposites

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Abstract

Graphite-oxide (GO) is an oxygen-rich carbonaceous material, typically obtained by the controlled oxidation of graphite. GO is a two-dimensional solid, with strong covalent bonding within the layers and weaker interlayer contact between intercalated water molecules. GO readily undergoes swelling and disaggregation and possesses an excellent intercalation ability and cation exchange capacity. In the present study, hydrophobic GO materials were prepared and utilized as host materials for Pd nanoparticles. Low-loaded organophilic Pd-graphite oxide nanocomposites were synthesized in micellar systems, by using the cationic surfactant tetradecylammonium bromide (C₁₄TAB) as a stabilizer. The samples were characterized by ICP-AES, XRD and TEM measurements. The catalytic performances of the samples were investigated for the liquid-phase hydrogenations of terminal and internal alkynes under mild conditions (101325 Pa, 298 K). It was established that a considerable portion of the Pd content of the Pd-graphite oxide nanocomposites was accommodated in the interlamellar space of GO, which was found to exert a crucial effect on the catalytic behaviour. The Pd/GO samples proved to be highly active and selective catalysts for the above reactions.

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Dry reforming of methane on Ni, Pt and NiPt/ZrO₂ catalysts: mechanistic studies with ¹³C labeled reactants

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Abstract

Nowadays methane dry reforming ($\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2$) has gained great attention in catalysis research. In the present work, activity of Ni, Pt and bimetallic NiPt/ZrO₂ samples with 1-3 wt% metal prepared by sol adsorption method or impregnation were investigated and compared in circulation system under sub atmospheric pressure (~50 mbar). Labeled reactants containing ¹³C were applied to trace the fate of carbon during either temperature programmed reaction or under isothermal conditions. The calcined and reduced fresh catalysts contained nanoparticles in the range of 2-10 nm according to the XRD, TEM and HRTEM measurements. Applying ¹³CO₂ + ¹²CH₄ as reactant mixture, formation of ¹³CO was seen prior (at lower temperature) to ¹²CO. This suggests that CO first detected in the gas phase originates from the activation of CO₂. Scrambling of labeled and unlabeled carbon species on catalyst surface was observed already at relatively low temperature. After the dry reforming reactions TPD of surface species retained by the catalysts revealed that in the case of Ni containing samples besides CO₂ and H₂, CO was detected, while from Pt samples CO was not desorbed at all. Surface carbon during the subsequent TPO measurements was removed only in the case of the above CO desorbing samples (Ni containing samples).

Acknowledgement

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ETHANOL STEAM REFORMING OVER ZnO AND ZrO₂ SUPPORTED Cu AND Ni CATALYSTS

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Abstract

Ethanol steam reforming is a promising reaction for hydrogen production. Ethanol can be considered as a suitable candidate for renewable hydrogen production as it can be produced by fermentation of glucose.

In this contribution we discuss the properties of ZnO and ZrO₂ supported Cu and Ni catalysts in terms of ethanol steam reforming. All samples with a total metal weight of 5% were prepared by impregnation of the oxide support material with Cu and Ni nitrate in aqueous solution. Besides monometallic Cu and Ni catalysts, bimetallic CuNi catalysts were prepared with a Cu:Ni ratio of 1:1. The samples were characterized using Temperature Programmed Desorption (TPD) of ethanol, both with MS detection of the desorbing gas molecules and during FTIR spectroscopy in order to obtain information about surface species. In addition, kinetic measurements with a gas chromatograph detection system were performed to study the activity, stability and selectivity of the different catalysts under ethanol steam reforming conditions (nEtOH:nH₂O= 1:3).

The results of TPD experiments showed that a higher amount of H₂ was produced on the monometallic Ni catalyst in comparison to the Cu catalyst. The bimetallic CuNi catalyst behaves like Cu at low temperatures, whereas at high temperatures this catalyst shows similar behavior as the monometallic Ni catalyst. Dehydration of ethanol to C₂H₄ was observed on ZrO₂ supported mono- and bimetallic catalysts whereas this was not observed on ZnO.

According to the FTIR-TPD experiments, a similar tendency of surface species is observed on all catalysts. At low temperatures the formation of ethoxy species is observed. With increasing temperature, formation of CO and different types of carbonates/acetates species occurs.

In the kinetic measurements a high activity for C-C bond cleavage (decomposition to CH₄, CO and CO₂) was detected on Ni. In contrary, a high selectivity to C₂H₄O (dehydrogenation) and to C₂H₄ (dehydration) was observed on Cu. The bimetallic catalyst shows a selectivity similar to Cu at low T and like Ni at high T. High stability was observed on CuNi catalyst compared to monometallic Cu and Ni catalysts. The H₂ yield is in the order: Ni > CuNi > Cu.

XPS characterization of CeO₂ and Al₂O₃ supported Co-Rh catalysts during the steam reforming reaction of ethanol

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Abstract

Since particular attention was devoted to hydrogen, a promising candidate for the environmentally friendly fuel of the future, several catalytic processes have been studied relating to hydrogen production. Although noble metals are active in the dehydrogenation of ethanol or ethanol-water mixture, their prices make the use of alternative catalysts more economical. Cobalt could be a possible substitute with or without the addition of noble metals. Recently it was shown that both Co/CeO₂ and Rh/CeO₂ catalysts are appropriate for producing hydrogen during the steam reforming process of ethanol. However, the highest hydrogen selectivity was obtained in the case of Rh doped Co/CeO₂.

X-ray photoelectron spectroscopy (XPS) was used to characterize the surfaces of CeO₂, Co/CeO₂, Rh/CeO₂ and Rh+Co/CeO₂ catalysts during the steam reforming of ethanol. After the pre-reduction a higher portion of Co was in the metallic state when the sample also contained Rh, but its total amount on the surface decreased due to either encapsulation by the support or diffusion to the lower layers. Rhodium was highly dispersed as demonstrated by the final state effect. During the reaction of ethanol, the amount of Co²⁺ decreased with increasing temperature. This process was accompanied by the severe reduction of ceria and the formation of significant carbon deposits. For comparison the ethanol steam reforming reaction was carried out over acidic Al₂O₃ supported Co catalysts. In this case the larger metallic particles were found to be more active in the reaction. However, Al₂O₃ opens a pathway towards ethylene formation.

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Preparation and photocatalytic activity of TiO₂-SiO₂ composite photocatalysts

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Abstract

Usage of colloidal suspensions of TiO₂ is very limited. The removal of nanoparticles from reaction system is almost impossible while keeping same properties of TiO₂. The preparation of TiO₂ nanocomposite seems to be a suitable solution of this problem. Another problem with the use of anatase is that the photocatalytic degradation is non-selective process and the binders or polymeric substrates are also degraded along with pollutants. The goal of this study is to find the way how to eliminate this problem. From the preliminary studies it results that the multicomponent nanocomposite materials based on combination of titanium dioxide and silica can be the suitable solution. TiO₂/SiO₂ composite materials were prepared from aqueous suspensions of each compound. Colloidal suspension of TiO₂ was prepared by hydrolysis of TiCl₄ at room temperature. As a source of SiO₂ the commercial product (Ludox AS30) was used. The TiO₂/SiO₂ composites were successfully prepared as a colloidal suspension and also as a powder, obtained from the precipitation of mixed TiO₂ and SiO₂ colloidal suspensions. It was confirmed that these composites are stable in suspension and they exhibit photocatalytic activity in aqueous media. Further, it was found that precipitation of prepared amorphous TiO₂ in the presence of SiO₂ leads to the crystallization of TiO₂ powder in anatase modification and prepared powder composites showed photoactivity in gaseous media.

Acknowledgement

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Electrochemical and Photoelectrochemical Characterization of Rutile Blocking Layers for Dye-sensitized Solar Cells

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Abstract

Dye-sensitized solar cells (DSCs) present an attractive alternative to solid state photovoltaics at competitive cost. An alternative to DSC is the solid state dye-sensitized solar cell (SSDSC). The SSDSC consists of FTO anode, TiO₂ film coated with a monolayer of dye molecules, an organic hole transporter and capped with a gold cathode. Recently dye molecules were replaced by methylammonium lead iodide perovskite and such SSDSC achieved more than 19% solar conversion efficiency.[1]

The recombination current over the FTO is relatively small in a liquid-type DSC, but not fully negligible, and it becomes crucial in the SSDSCs. For their proper function, a nonporous blocking underlayer of TiO₂ must be deposited on top of FTO to prevent shunting of electrons from the FTO support to the hole-transporter.[2] This layer is usually fabricated by spray pyrolysis but there are various other synthetic protocols. One of them is magnetron sputtering, physical vapor deposition technology that is used to grow many types of thin films on various substrate materials.

The aim of this work was preparation of rutile thin transparent dense layers by hybrid high-power impulse magnetron sputtering (HiPIMS), their characterization (photoelectrochemical and electrochemical measurements) and evaluation of their blocking properties.

Acknowledgement

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Wacker oxidation of ethylene over Pd/V-SBA-15 catalysts

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Abstract

Acetaldehyde is industrially synthesized by Wacker-type homogeneous oxidation of ethylene with O_2 in system containing aqueous solution of HCl , $PdCl_2$ and $CuCl_2$. The homogeneous reaction suffers from several drawbacks, such as, the high corrosivity of the reaction mixture, formation of chlorinated by-products, depletion of palladium, leading to loss of catalytic activity, and that the process gives off noxious copper-containing waste. To overcome disadvantages studies has been launched to develop solid catalysts by immobilization of an active complex to a surface of an inert support. It was recognized that besides copper, vanadia can also act as co-catalyst of Pd in heterogeneous Wacker catalysts. In present study we describe three routes for the preparation of vanadium-containing SBA-15 silica materials (V-SBA-15), namely, the impregnation of the support by NH_4VO_3 , the selective reaction of surface hydroxyls with vanadyl acetylacetonate, and the SBA-15 synthesis, having vanadium source ($V_2O_5+H_2O_2$) in the synthesis gel. To obtain Wacker catalysts the V-SBA-15 samples were impregnated by Pd salt in a further step. The catalysts were analyzed by ICP, their structure and morphology was characterized by XRD, TEM and N_2 -adsorption measurements. H_2 -TPR measurements were carried out to learn about the reducibility of the vanadia forms. The connection between selectivity towards partially oxidized products of ethylene and the electronic structure of the VO_x species in the V-SBA-15 materials was examined by *in-situ* UV-vis technique.

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Microscopic characterization of changes in the structure of the KCo/CeO₂ catalyst during steam reforming of ethanol

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Abstract

Shortage of fossil fuel in the near future will cause serious energy problems. Hydrogen is a clean energy source and its demand as a fuel for fuel cells is increasing. The steam reforming of ethanol (SRE) is an effective method of hydrogen production. Potassium promoted Co/CeO₂ catalyst in view of the high effectiveness of ceria oxide used as a support and the low cost of cobalt can form a highly active and selective catalytic system proposed for the SRE.

Structural and chemical characterization at the atomic scale becomes a vital requirement in order to identify structure–performance relationships existing in heterogeneous catalyst systems. In recent years characterizations of heterogeneous metal catalysts have been greatly improved by the use of modern chemical-physical research methods, such as electron microscopy coupled with other analytical techniques.

In this study potassium promoted cobalt catalyst with a CeO₂ support was prepared by an impregnation method and used in the SRE. The catalyst was characterized in its oxide form and after work in the SRE by electron microscopy methods and EDS. Microscopic characterization of the catalyst allowed us to identify the cobalt active phase (in Co₃O₄ form) and the CeO₂ support phase (O-terminated), existing in the fresh catalyst, and also active phase (in different forms), support CeO₂ phase and carbon phase in the used catalyst. STEM-EDS studies allowed us to determine distribution of all components in the catalyst as well as carbon in the catalyst used in the SRE. Microscopic studies of the used catalyst proved that its surface was covered with various carbonaceous deposits, which were the main reason of deactivation of the catalyst. Post-reaction TEM/STEM images of the catalyst reveal three types of carbon configurations: fibers, encapsulates and partly surrounding carbon.

Comparative study of MCM-22 and MCM-56 modified with niobium, zirconium, and molybdenum

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Abstract

Multilayer MCM-22 and delaminated MCM-56 are members of MWW zeolites family. The differences in their structure affect surface properties. Both zeolites are acidic catalyst and modification with metals gives opportunity to obtain bifunctional (acid-redox) catalysts. The objective of this study was the comparative examination of MCM-22 and MCM-56 zeolites modified with Nb, Zr and Mo species. The structure/texture and surface properties as well as catalytic activity in dibutyl sulphide (Bu_2S) oxidation with H_2O_2 were compared for the two types of zeolites. Various characterisation techniques and test reactions applied in this study confirmed strong acid character of zeolites prepared. The presence of Brønsted (BAS) and Lewis (LAS) acid sites were detected after pyridine adsorption. The difference was in the number and strength of BAS and LAS which reflects the activity and selectivity in liquid phase Bu_2S oxidation with H_2O_2 . In the absence of catalyst the conversion of Bu_2S reached 78 % after 8 h. The application of HMCM-22 zeolite significantly increased the reaction rate (100 % conversion after 5 h) because of LAS presence in this sample. LAS are responsible for Bu_2S chemisorption which is the first step in catalytic reaction. For HMCM-56 the growth of activity was not registered. Modification of HMCM-22 with Mo and especially with Nb significantly increased the activity (100 % conversion after 15 min and ca. 90 % selectivity to sulfoxide on Nb/MCM-22). Interestingly, Nb/HMCM-56 exhibited enhancement of both, conversion (90 %) and sulfoxide selectivity (90 %). Modification of both zeolites with Zr did not enhance the activity. The spectacular role of Nb species is due to its interaction with H_2O_2 towards peroxo/superoxo species. The relationship between the nature of metal and the zeolite structure and activity will be detailed discussed.

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The effect of lanthanum content on the properties of cobalt catalysts in NH₃ synthesis

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Abstract

The industrial process of NH₃ synthesis has a significant value for today's society. It is estimated that without the production of ammonia, only 60% of the global population could be nourished. Thus, the matter of improvement of the ammonia synthesis efficiency has attracted many researchers. New catalysts for NH₃ synthesis may be cobalt systems, where the essential components are promoters.

This work studies the promoted cobalt catalysts obtained by coprecipitation. The attention is focused on the influence of lanthanum content on the properties of the prepared cobalt systems, especially their catalytic activity. The lanthanum content in the obtained materials was in the range 0-55.7 wt.%. The samples were characterized by N₂ physisorption, XRPD, SEM, TPR and H₂ chemisorption. The activity of the catalysts in NH₃ synthesis was measured in a flow differential reactor operating under steady-state conditions ($p = 6.3$ MPa, $T = 370$ - 430°C , $\text{H}_2:\text{N}_2 = 3:1$).

The obtained results revealed that lanthanum is an effective promoter of cobalt catalysts. In the investigated systems lanthanum plays the role of a structural promoter. The increase of lanthanum content causes the increase of the active phase surface (metallic Co) and its activity in NH₃ synthesis. However, a negative effect of lanthanum addition on the reduction of the active phase was also observed.

The Al, Ga, In salts of tungsten and molybdenum heteropolyacids - theory vs. experiment.

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Abstract

The paper presents studies on mono-cationic salts of molybdenum and tungsten heteropolyacids, with general $M_3PMo_{12}O_{40}$ (MPMo) and $M_3PW_{12}O_{40}$ (MPW) formula (where M = Al, Ga, In). Theoretical modeling was performed with DFT theory, used both cluster (Turbomole program) and periodic (VASP program) approaches. Determination of the activity of heteropolyacid salts was done in a model reaction i.e. the conversion of ethanol in the gas phase. Results of theoretical calculations performed for Mo and W mono-cationic salts within periodic model showed the differences in redox properties: for each cation, the width of band gaps in MPMo is smaller than in MPW. Theoretical results correlate with experimental data which show that acetaldehyde, being a product of redox reaction, is formed only on MPMo salts. Creation of acidic sites in studied systems were modeled within cluster DFT approach, based on the mechanism proposed in the literature [1], where hydrated cation turns into hydroxylated cation with liberation of water and protons. Quantum-chemical calculations carried out for cation aqua-complexes of different coordination numbers ($n=2-6$) and systems where cations are linked to three water molecules and connected with Keggin anion, indicated that energetically the most favorable reaction pathway leads to formation of di-hydroxyl species and two protons. Energy of proton formation has a direct impact on the number of acid sites defining the Bronsted acidity of the systems which decreases in the order $Ga > In > Al$. known from the experiment.

Hydrotalcite derived bi-functional catalysts for low-temperature selective oxidation of ammonia to nitrogen

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Abstract

Many chemical processes use ammonia as a reactant or produce ammonia as a by-product (e.g. nitric acid and nitrogen fertilizer production, urea manufacturing, hydrodenitrification process, DeNOx process). Ammonia is a toxic compound and therefore their emission into atmosphere can result in degradation of environment. The selective catalytic oxidation (SCO) of ammonia to nitrogen and water vapor ($4\text{NH}_3 + 3\text{O}_2 = 2\text{N}_2 + 6\text{H}_2\text{O}$) is one of the most promising methods for the removal of toxic NH_3 from oxygen containing waste gases. For this process a mechanism of internal selective catalytic reduction (i-SCR) consisting of two steps was proposed. In the first step ammonia is oxidized to NO, while in the second step NO is reduced by ammonia, unreacted in previous step, to N_2 and H_2O .

The presented studies are focused on development of active and selective bi-functional catalysts for the SCO process. Selected noble metals (Pt, Pd, Rh) play a role of components active in the oxidation of ammonia into NO, while hydrotalcite derived mixed metal oxides containing copper and iron were used as components active in the reduction of NO with ammonia. The results of the catalytic studies showed that deposited noble metals significantly activated hydrotalcite derived catalysts for the low-temperature SCO process but also increased selectivity of ammonia oxidation to undesired nitrogen oxides. [1].

[1] L. Chmielarz, M. Jabłońska, Z. Piwowska, A. Węgrzyn, S. Witkowski, M. Michalik, Appl. Catal. B 130-131 (2013) 152-162.

Remarkable effect of soft – templating synthesis procedure on catalytic properties of mesoporous carbon supported Ni in hydrodechlorination trichloroethene in liquid phase

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Abstract

Water is one of the most important substance in the world but the access to the clean resources becomes problematic due to e.g. contamination of ground and drinking water by volatile organic compounds (VOC's), like chlorinated hydrocarbons. Attractive, environmentally friendly, method of “utilization” of these chemicals is hydrodechlorination (HDC), especially because catalytic HDC is considered to be one of the most universal resource-saving methods for reprocessing chlorinated hydrocarbons. The aim of this work was to investigate properties of two mesoporous carbon supported nickel catalysts in hydrodechlorination of trichloroethylene (TCE) in drinking water.

2wt.%Ni/C catalysts were prepared by two different procedures: incipient – wetness impregnation of mesoporous C_{ST-A}, prepared by the soft - templating method under acidic conditions, by nickel chloride solution; and the second one was prepared directly by the soft - templating method. The catalysts were characterized by different methods e.g. Temperature - Programmed Reduction (TPR), hydrogen chemisorption, Transmission Electron Microscopy (TEM), and X-ray diffraction (XRD). Both mesoporous carbons supported nickel catalysts have shown an excellent properties in purification of water from trichloroethylene without presence of an additional organic solvent in the reaction mixture.

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Influence of the carrier on physicochemical and catalytic properties of Cu-Ag/oxide catalysts for selective hydrogenolysis of glycerol to propylene glycol.

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Abstract

Hydrogenolysis of glycerol to propylene glycol using bifunctional catalysts is a catalytic reaction, which allows to obtain PG in a way that is environmentally and economically attractive - compared to the conventional method of production from petroleum derivatives. Due to its physicochemical properties and wide range of applications in various industries, propylene glycol is one of the most interesting compound possible to obtain from waste glycerin phase formed in the production of biodiesel.

Two series of catalysts containing active copper phase modified by silver were synthesized by wet impregnation method using water solutions of copper and silver nitrates, followed by drying (120°C, 10 h) and calcination in the air flow (350°C, 5 h). The TiO₂ and acidic Al₂O₃ oxides were used as supports. In order to determine the physicochemical properties of the prepared catalysts, measurements of TPR-H₂, BET, XRD and XRF were conducted.

The catalytic tests were carried out in a "batch" reactor with mechanical stirring (process conditions: 200°C, 5 h, stirring speed 400 rpm, 15 atm. of hydrogen pressure). Hydrogenolysis reactions were preceded by reduction of the catalyst in each case (150°C, 2 h, stirring speed of 100 rpm, 2 atm. of hydrogen pressure). Then the above reaction and reduction parameters were modified in order to optimize the conditions.

On the basis of the physicochemical characterization, the silver addition modifies the properties of copper oxide and affects the surface area of the obtained catalysts.

Catalysts, wherein the carrier is Al₂O₃ are more active in the hydrogenolysis reaction of glycerol and much more selective to the 1,2-propanediol than their analogs containing TiO₂ as the carrier. Optimization of the reaction conditions leads to the conclusion that the reaction time and hydrogen pressure are the key parameters of glycerol hydrogenolysis. Modification of the reaction parameters allowed to increase both the glycerol conversion and selectivity to 1,2-propanediol.

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Sorbitol dehydration in a ZnCl_2 molten salt hydrate medium: a molecular modelling study.

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Abstract

A molecular modelling study, using standard DFT B3LYP/6-31G*, was carried out to develop a better understanding of sorbitol dehydration into isosorbide in ZnCl_2 molten salt hydrate medium. Catalysis of sorbitol dehydration by ZnCl_2 most likely starts with complexation of the sugar alcohol functions to Zn, followed by an internal $\text{S}_{\text{N}}2$ mechanism of a secondary alcohol function attacking a primary alcohol function with the Zn-complex acting as a favourable leaving group. The dehydration reactions to 1,4- and 3,6-anhydrosorbitol show a very similar activation barrier in good accordance with experimental results. The same holds for the formation of isosorbide from 1,4- and 3,6-anhydrosorbitol, albeit with a slightly higher activation barrier. The relative level of the activation barriers reflects the increased strain in the sorbitol skeleton in the corresponding transition states. ZnCl_2 turns the dehydration reaction from an endothermic one to an exothermic one by forming a strong complex with the released water. Finally, the $\text{ZnCl}_2\text{-H}_2\text{O}$ system has been compared with $\text{HCl-H}_2\text{O}$, which could have been an alternative; it, however, turned out not to be the case.

Novel on-stream modification strategy of MFI zeolite membranes for improving their selectivity

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Abstract

Advances in membrane materials and their fabrication technology are, among many potential solutions, one of the most direct, effective and feasible approaches technologies for solving key issues in both energy and environmental emerging systems. Complex membrane architectures are being developed in our Institute with oxides, non-oxides, hybrid or composite materials, and new reaction pathways are also investigated to orient the formation of stable material designs. An important part of the research activity in our group is currently focussed on zeolite membrane due to their specific properties coupling attractive functionalities such as adsorption/separation & catalytic activity which could be advantageously applied in the treatment, separation and/or filtration of gases and vapors. The principal bottleneck of zeolite membrane bears on an unavoidable formation of intercrystalline defects during the synthesis and poor molecular sieving effect limiting their industrial applications. Number of strategies have been already reported in the literature for producing zeolite membranes with a reduced number of irregularities, with tailored inter-/intra-crystalline pathways and/or with specific adsorption or catalytic activity.

In this work we report on both *in-situ* and *ex-situ* modifications of MFI zeolites, for preparing membranes with enhanced efficiency for gas separation or catalytic reactor applications. A special attention will be paid to an original post-synthesis modification strategy in supercritical CO₂ (scCO₂). This novel modification method is based on a controlled transport/infiltration of specific alkoxides into a zeolite membrane followed by their catalytic cracking leading to a blocking of the MFI intercrystalline pathways and/or a reduction of zeolite channel size for increasing membrane selectivity while maintaining high permeance.

The application of this method open the way to a large range of (green) strategies for the controlled modification of zeolite membranes by using on-stream methods.

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From porosity to catalytically active site

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Abstract

Understanding the mechanism of a catalytic reaction is essential for design of new and better processes. However, it remains difficult to capture the structure of a catalytic site as the majority of atoms are inactive and they often dominate the spectroscopic signal. Thus measuring the averaged structure of a catalyst, even if it is under catalytic conditions, does not yield the desired structure – performance relation. One solution is to measure catalyst structure in a time resolved manner after modification of the reaction conditions. Such transient experiment may yield the actual structure of the ensemble of atoms that constitute the catalytically active site. I will present the occurrence of transient phases in supported noble metal catalysts in oxidation of carbon monoxide and the kinetics of formation based on X-ray absorption spectroscopic signals.

Knowledge of the structure of the active site is insufficient to develop new catalysts. An essential requirement of a catalyst is that reactants can reach the active site and products diffuse away. It is crucial that catalyst bodies are sufficiently porous. Characterization of catalysts in three dimensions is needed to relate pore size distribution to pore connectivity and eventually performance. I will describe recent developments in the analysis of porosity of catalysts in three dimensions sub-micrometer length scale. Composite catalysts of zeolite-binder, which is the most-used catalyst in oil refining, the FCC catalyst, will be given as example.

New types of Pt-GaN/ZnO photocatalysts for hydrogen production

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Abstract

Photocatalytic hydrogen production is a promising approach for storing solar energy as chemical energy. Furthermore hydrogen can be efficiently transformed into electricity without environment pollution in fuel cells. In order to effectively utilize solar energy, new materials working under visible light are needed. Recently GaN/ZnO solid solutions obtained by high temperature nitridation of the mechanical mixture of Ga₂O₃ and ZnO have been used for decomposition of H₂O into H₂ under visible light irradiation. However the zinc is volatile so the composition of the solid solution strongly depends on the temperature and duration of the NH₃ treatment. Our aim was to find new preparation methods for GaN/ZnO solid solution and Pt-GaN/ZnO photocatalyst system. It is known that the deposition of noble metal nanoparticles such as Pt on the surface of the semiconductor successfully prevents the recombination of the photogenerated electron-hole pair increasing the efficiency of a photocatalyst. Homogeneous distribution of precursors on molecular level is believed to be favorable to form the solid solution at relatively mild conditions; therefore co-precipitation, sol-gel technique and application of chelating agent were used in our approach. The Pt co-catalyst was loaded by impregnation and in situ hydrogenation with NaBH₄. A comparison of the catalysts prepared by different methods will be given in the presentation.

Acknowledgement

This project has been supported by the National Development Agency, grant No. KTIA_AIK_12-1-2012-0014. Financial support by the OTKA-project K77720 (András Tompos) and K100793 (Zoltán Pászti) is greatly acknowledged.

Deposition of hematite thin films by DC pulsed magnetron sputtering

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Abstract

Iron oxide (α -Fe₂O₃) in hematite crystalline structure has been extensively examined for application to solar water splitting using photoelectrochemical cells due to its high chemical stability, nontoxicity, abundance, ability to absorb within the significant part of the solar spectra, and the low cost. We report on preparation of hematite thin films by means of reactive magnetron sputtering in several pulsing modes together with so called high power impulse magnetron sputtering (HiPIMS) regime. Three pulsing frequencies of the magnetron discharge including 100 Hz, 1 kHz with “on” time 100 μ s and 50 kHz with “on” time 15 μ s were investigated. It was revealed using Raman spectroscopy and XRD that all these frequencies provided crystalline films with the hematite phase already during the coatings. For each particular pulsing frequency, however, a different orientation of crystallites was found, which was verified by Mössbauer spectroscopy. The films were also characterized using a broad range of methods (XRD, Raman spectroscopy, XPS, spectroscopic ellipsometry, AFM, SEM, etc.). The solar photocurrent measurements were done to assess the photoelectrochemical performances of the hematite electrodes.

Iron and molybdenum catalysts for propylene oxidation: the effect of metal-support interactions

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Abstract

The catalytic effects of supported mono- and bimetallic iron and molybdenum-based catalysts on the selective oxidation of propylene in gas phase have been studied. Nitrous oxide, as well as air were used as oxidizing agents. For both metals, several specific forms of metal oxide nanoparticles have been identified by TEM and voltammetric techniques. The textural and electrochemical properties of these catalysts correspond well with their catalytic activities, the different metal oxide species directing the oxidation toward a selective formation of propylene oxide, or toward the products of allylic oxidation, or toward undesired CO_x, respectively. It have been equally found that by tuning the preparation methods properly – e.g. by addition of further modifiers or by changing the atmosphere during the catalyst preparation – it is possible to prepare preferably a targeted form of metal oxide nanoparticles.

A correlation between the epoxidation activity and transition-response experiments, found in the framework of the present study, allows a prediction of the catalytic activity of the Mo- and Fe-based catalysts. An XPS-characterization elucidates further the chemical reactions and diffusion-controlled processes taking place during the calcination of the catalysts, determining their final activity in propylene oxidation.

Engineering aspects of catalysis in microreactors

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Abstract

Microreactors are said to be very efficient tools for the process intensification and kinetic and mechanistic studies of many types of catalyzed reactions. Is this really true or are there also any disadvantages of this approach? Are the microreactors the universal solutions or should we expected difficulties during their implementation in the given process? Is the scale-up of microreactors as simple as advertised? Is micro always better?

We will try to answer these and similar questions by giving examples of several cases, in which we studied microreactors in relation to different catalytical systems. The presented cases will include the heterogeneously catalyzed gas phase reactions (oxidation of SO₂, hydrogenation of 2-methylpropene), heterogeneously catalyzed enzymatic glycerolysis of vegetable oil, photochemical debromination of PBDE, and homogeneously catalyzed photochemical oxidation of 4-chlorophenol. We will present some surprising results and comparisons with conventional reactors.

Enhanced visible light photocatalytic activity of Pt/I-TiO₂ and Pt/I-, C-doped TiO₂

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Abstract

Titanium (IV) oxide (TiO₂) is one of the most important photocatalytic materials in the area of environmental purification, hydrogen generation and CO₂ photoconversion to methane and low hydrocarbons. In order to use green, abundant and cheap solar energy many attempts have been made to improve the optical response of TiO₂ under visible light irradiation. Doping of nonmetal ions (e.g., N, S, C, F, etc.) into the TiO₂ lattice create intra-band-gap states close to the conduction or valence band edges that induce visible light absorption. Additionally, substitution of a titanium atom with iodine leads to generation of Ti³⁺ that may trap photoinduced electrons and inhibit charge recombination. In this work, Pt/I-TiO₂ and Pt/I-, C- doped TiO₂ photocatalysts were prepared with iodine and/or carbon doped into the TiO₂ lattice and Pt deposited on TiO₂ surface. The incorporation of platinum ions and iodine/carbon leads to enhanced photocatalytic activity as compared with single ion-doped TiO₂. Platinum is one of the most active metals for photocatalytic enhancement which facilitate electron capture and hinder the recombination rate between electrons and holes. Platinum modified and iodine-, carbon co-doped TiO₂ nanoparticles (Pt/I-, C-TiO₂) were prepared through a combined hydrothermal and wet-impregnation method. Obtained photocatalysts were characterized using XRD, TEM, XPS, UV-Vis absorption spectroscopy and BET surface area analysis. The effect of platinum modification and non-metal precursor and its amount on the photocatalytic activity of I-, C-doped TiO₂ was investigated.

Acknowledgement

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Fe-amino acid complexes, immobilised on silica gel, as active and highly selective catalysts in cyclohexene epoxidation

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Abstract

In this work the syntheses, structure, superoxide dismutase (SOD) activity and the catalytic use in the oxidative transformations of cyclohexene of covalently grafted Fe(III)–complexes formed with various C-protected amino acid (L-histidine, L-tyrosine, L-cysteine and L-cystine) ligands is presented. The structural features of the surface complexes were studied by XANES/EXAFS and mid/far IR spectroscopies. The compositions of the complexes were determined by ICP-MS and the Kjeldahl method. The superoxide dismutase activities of the materials were evaluated in a biochemical test reaction. The obtained materials were used as catalysts for the oxidation of cyclohexene with peracetic acid in acetone. Covalent grafting and building the complex onto the surface of the chloropropylated silica gel were successful in all cases. It was found that in many instances the structures obtained and the coordinating groups substantially varied upon changing the conditions of the syntheses. All the covalently immobilised Fe(III)–complexes displayed superoxide dismutase activity and could catalyse the oxidation of cyclohexene.

Acknowledgement

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Analytical Methods for the Characterization of Pt-Rh Catalyst

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Abstract

The Pt-Rh catalyst in the form of standard sieve catalyst which is used for a very long time in the manufacture of nitric acid and other chemical technologies. It is characterized by a high mechanical strength at high operating temperatures, high resistance to catalyst poisons and considerable efficiency. The content of rhodium in the catalyst system Pt-Rh ranges from 5 to 10% depending on the use of catalyst and the price of rhodium. In some cases, used Pt-Rh catalysts may at certain conditions reduce the catalytic activity and thus reduce the product yield significantly. The reasons of these unexpectedly low yields are often very complex. The contamination of Pt-Rh catalyst can be mainly caused by: 1) the purity of process gases, 2) the reactor construction materials, and 3) the purity of catalyst gauzes. A special attention has to be paid to the presence of contaminants during the start-up period. The contamination during the start-up period causes an incompletely developed crystal structure. The contamination in this period greatly reduces the yield of the process in the campaign. The present study deals with the determination of textural and surface changes in the catalytic sieve after use. We can conclude that the scanning electron microscopy (SEM) with microanalysers (EDAX) and (EDX), has been the most suitable and most commonly used analysis for a quick identification of problems with the catalytic converter. Using this method can promptly and reliably determine the morphology of catalyst composition, and surface contaminants. To enhance the chemical composition X-ray fluorescence analysis (XRF) can be used. For a detailed monitoring of the morphology of catalytic screen Auger spectroscopy (AES), secondary ion mass spectrometry (SIMS) and optical emission spectrometry with inductively coupled plasma (ICP-OES) can be applied. Raman spectroscopy methods have not been suitable for this system.

A Case Study in Specific Surface Area of Nanoparticles ZnO

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Abstract

Zinc oxide has many uses. Nanoparticles of zinc oxide could be applied for example as a pigment, photocatalyst or as a rubber additive. Almost in the half of world zinc oxide is used as an activator for vulcanization accelerators in natural and synthetic rubber. The reactivity of zinc oxide is a function of its specific surface area. Zinc oxide of high specific surface area can be produced industrially from purified solutions of zinc sulfate or chloride by various techniques. For example, the solutions of sodium hydroxide, sodium carbonate, ammonium carbonate, urea etc. can be used as the precipitating agent. The resulting precipitate is then washed, filtered, and finally calcined.

In this study, we wanted to investigate the conditions for measuring of adsorption isotherms of these types of materials. Equilibrium adsorption isotherms of nitrogen were measured at 77 K using static volumetric adsorption systems (ASAP 2020 or ASAP 2050 analyser, Micromeritics). The adsorption isotherms were fitted to produce the BET surface area, the micropore volume was derived by the t-plot method and the pore size distribution by model distribution of mesopores for cylindrical pore geometry based on the Barret, Joyner and Halenda (BJH method) and density functional theory (DFT method). The BET surface area of precipitated ZnO nanoparticles was in the range 3 – 100 m²/g. The pore size distribution results showed that zinc oxide was predominantly mesoporous. It was observed that the median pore size of the zinc oxide nanoparticles was in the range from 5 to 35 nm (pore diameter).

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Influence of lanthanides on decomposition of metazachlor

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Abstract

Doped titanium dioxide was prepared by a sol-gel synthesis and consequently by using solid state reaction at temperature 450 °C. Titanium(IV)isopropoxide was applied as a precursor, isopropanol as a solvent and acetylacetone as a stabilization agent. Titanium dioxide was doped by praseodymium, dysprosium, and ytterbium ions; and the influence of these lanthanides on photocatalytic activity was evaluated. Crystallite phases were analyzed by X-ray diffraction (Rigaku) using Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation in the scan range from 2θ from 15° to 100°. Pure anatase was obtained in all cases. Thermal decomposition was studied by thermogravimetric analysis and specific surface area (BET) was calculated from N₂ adsorption/desorption measurement. The band gap energy of all samples was examined from diffused reflection spectra. The morphology of prepared powders was investigated by scanning electron microscopy (SEM) accompanied by X-ray dispersive spectroscopy (EDS) for determination of chemical composition.

Photocatalytic activity of all doped titania photocatalysts was explored as a degradation rate of metazachlor, common used herbicide. The influence of lanthanide dopants on photocatalytic activity was investigated.

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Dopant ions in the framework of parent zirconia for the Pt/WO₃-ZrO₂ catalysts preparation

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Abstract

From discovery of WO₃-ZrO₂ catalysts providing high isomerization activity for n-paraffins into required iso-paraffins conversion, a large amount of research work has been devoted to analyze the preparation and resulting catalytic properties of this type of catalyst. Among numerous phenomena including the formation of active species, and/or the preparation of starting material from amorphous and/or crystalline ZrO₂ was studied. The aim of this report is to show that use of starting ZrO₂ with implanted metal ions modify the catalytic properties of resulting Pt/WO₃-ZrO₂ and improve the isomerization activity for paraffin skeletal isomerization. It could be summarized that using optimal amounts of several metal cations as dopants of the Pt/WO₃-ZrO₂ catalysts the C₆ and C₇ isomerization activity of the catalysts at T>250°C could be improved. Among Al, Si, Fe metal dopant ions, the Al-dopant was demonstrated to be the most effective. The role of difference between surface-doping and framework doping by Al-dopant ion was also studied, by various techniques, and framework doping shown as the most effective way to improve isomerization activity. This effect is probably caused by formation of defect structure of the parent ZrO₂, which then play a key role in surface formation of WO_x species optimal for paraffin activation during the isomerization process.

Acknowledgement

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Catalytic oxidation in micro-photo-reactor system

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Abstract

Micro-reactor technology is actually used as a trend in the area of chemical, especially in the pharmaceutical industry for high quality and the cleanness of products. The main advantage of this method is the safety of chemical processes, the assurance of the temperature stability and the significantly low environmental impact. Micro-reactor system as the continual process seems to be promising as an alternative to the large batch reactors. Time saving, lower cost, the wide applicability easier scale-up are another advantages of micro-reactors. Catalytic photo oxidation processes have been studied in the micro-photo-reactor system (Ehrfeld Mikrotechnik BTS). This work is focused on the partial oxidation of benzaldehyde to benzoic acid as a model reaction.

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Synthesis of 3D porous nanocarbon with defined structure

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Abstract

The microporous and mesoporous carbon materials are interesting for their wide application in electrodes, fuel cells, catalysis, adsorption, gas separation, and water and air purification processes. The study aims into synthesis of 3D porous nanocarbon materials with high surface area ($\geq 2000 \text{ m}^2 \cdot \text{g}^{-1}$), and with defined architecture and dimensions of micro-mesoporous structure. The main effort was centred on synthesis of carbon materials using BEA and Y zeolites as hard templates and the chemical vapour deposition with propylene as a carbon precursor. Synthesis of nanocarbon materials was performed using carbonization of the microporous and micro-mesoporous zeolites in a propylene stream at temperatures from 750 to 850 °C, followed by dissolution of the zeolite framework with HF and HCl acids. Microporous zeolites were employed to obtain 3D porous nanocarbon with unified porous structure formed by an inverse replica of zeolites channel system. Micro-mesoporous zeolites as hard templates were used to shorten the length of micropores in 3D porous nanocarbon and thus enhance mass transport in the defined channel structure. Structure of prepared carbon materials was analysed by using XRD, XPS, SEM and adsorption of N₂. In this study, we optimised the synthesis procedure for effective replication of the channel structure of BEA and Y zeolite into carbon providing 3D porous nanocarbon materials with surface area of $2\,500 \text{ m}^2 \cdot \text{g}^{-1}$, and suggested and developed a new synthesis procedure for 3D micro-mesoporous nanocarbon materials.

Acknowledgement

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Study of mechanism of amines conversion on hydrogenation catalyst surfaces by temperature-programmed desorption

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Abstract

Catalysts based on transition metals are used particularly in hydrogenation-dehydrogenation processes. The aim of this work was to contribute to a deeper understanding and clarification of amines transformation (*n*-butylamine, dibutylamine, tributylamine) on heterogeneous metal catalysts (Pt/SiO₂, Pd/SiO₂, Co/SiO₂, Ni/SiO₂, Cu/SiO₂).

The range of chemical reactions accompanying desorption has been studied by the technique of temperature programmed desorption (TPD) in a carrier gas stream at temperatures up to 200 °C, which are the characteristic hydrogenation temperatures. TPD spectra were measured using a commercial apparatus for temperature programmed techniques AutoChem II 2920 coupled with a quadrupole mass spectrometric system for online analysis MKS Cirrus II.

Measuring TPD spectra of studied amines on the metal catalyst surface was carried out in a stream of inert gas (He) or hydrogen atmosphere. It was clarified which reactions accompany desorption of amines from the surface of said catalysts.

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Notes on limonene isomerization

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Abstract

This study deals with limonene isomerization to monoterpene products (terpinolene, α -terpinene, γ -terpinene, β -terpinene, α -phellandrene, β -phellandrene, 2,8(9)-p-menthadiene, 2,4-p-menthadiene) using different types of catalysts. All of these terpenes are desirable in perfume industry as intermediates; especially β -terpinene and β -phellandrene with exocyclic double bond are desirable. Usual catalyst for limonene isomerization is sulphuric acid and solid catalysts based on $\text{SO}_4^{2-}/\text{SiO}_2$. Interesting and promising isomerization catalysts are heteropoly acids anchored on zeolites.

The influence of catalyst type, amount of heteropoly acid on support, zeolite (support) type, calcination temperature, reaction temperature on product composition in limonene isomerization was determined. Detail catalyst characterization was performed and the results were compared with catalyst properties, especially acidity. Catalyst acidity has the highest influence on product composition - high amount of strong Brønsted acid sites lead to disproportionation of limonene producing p-cymene and p-menthene. Low amount of acid sites lead to the formation of terpinolene and terpinenes.

Cyclamenaldehyde synthesis: aldol condensation followed by hydrogenation over ruthenium catalyst

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Abstract

Cyclamenaldehyde is a fragrant substance with the scent of cyclamen or lilly-of-the-valley. It is used in detergents and perfumes to replace its analogue – Lily aldehyde, which was classified as a possible mutagenic agent and its use is going to be forbidden. In this work desired cyclamenaldehyde was prepared by two-step synthesis.

At the first step aldol condensation of 4-isopropyl benzaldehyde and propanal was carried out. The influence of used catalyst (kalium hydroxide and sodium methoxide) and propanal amount was tested. Propanal was used in excess and added to the reaction mixture dropwise to prevent its self-condensation to 2-methylpent-2-enal. Resulting mixture of 4-isopropylbenzaldehyde and forcyclamenadehyde was hydrogenated using different Ru/C catalysts. The products detected in hydrogenation reaction mixture were: desired cyclamenaldehyde, cyclamenalcohol and forcyclamenalcohol. The influence of catalyst type and amount, reaction temperature and hydrogen pressure on the reaction course was tested.

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Framework Al-Lewis sites in zeolites. $^{27}\text{Al}\{-^1\text{H}\}$ REDOR (3Q) MAS NMR and QM/POT study of perturbed Al atoms

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Abstract

Zeolites are crystalline microporous aluminosilicates made of corner-sharing TO_4 tetrahedra ($\text{T} = \text{Si}, \text{Al}^-$). They represent a very important group of industrial heterogeneous catalysts. Their protonic forms serve as acid catalysts for hydrocarbon transformations. Brønsted acid sites Si-OH-Al are the corresponding active sites. Besides them, framework as well as extra-framework Lewis electron-pair acceptor sites can be present in the catalyst. The former most likely correspond to perturbed framework Al sites, but their detailed structure is still unclear. The latter are attributed to octahedrally coordinated Al species. Local structure of framework Al-Lewis sites and perturbed framework Al atoms in three ferrierite zeolites with Si/Al 8.5, 9.0 and 21 and two chabazite samples with Si/Al 2.0 and 3.5 zeolites was studied by ss-NMR and QCH calculations. Perturbed Al atoms are characterized by ^{27}Al resonance with $C_Q = 5$ MHz and $\delta = 62$ ppm and correspond to the framework Al with terminal Al-OH group. The Al-OH species represents a precursor of framework Al-Lewis site formed by their dehydroxylation giving three coordinated framework Al. The formation of $(\text{SiO})_3\text{Al}$ Lewis site is reflected in the extremely broad ^{27}Al resonance with predicted values of $C_Q = 35$ MHz and $\delta \approx 67$ ppm in the $^{27}\text{Al}\{-^1\text{H}\}$ REDOR MAS NMR spectrum.

Homogeneous transfer hydrogenation in capillary microreactor – comparison with batch process

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Abstract

Microreactor systems are intensively developing systems playing the key role for the intensification of manufacturing processes as well as for the increase in safety in many branches of academy, science and industry. Especially fine-chemical and pharmaceutical industries require products of predefined purity, which can be secured by the use of the microfluidic flow systems. These systems typically have at least one internal characteristic dimension below 1 mm. Primary positive feature of these systems is their high active surface to reaction volume ratio ensuring the proper control of reaction conditions and high heat, mass and momentum transfer. This is one of the most necessary facts for the performing of fine-chemical synthesis. Nowadays, still increasing interest is attached to the asymmetric catalytic transfer hydrogenations of β -keto esters represented by the model reaction - hydrogenation of methyl acetoacetate to methyl hydroxybutyrate. This reaction is catalysed by the Noyori-Type Ru-BINAP catalyst, chemically *[(R)-(2,2'-bis(diphenylphosphino)-1,1'-binaphthyl)ruthenium(II)chloride]*. It ensures the reaction to be catalysed enantioselectively resulting in products of predefined purity with no need of subsequent cleaning or even separation. For the increase of safety, 2-propanol was chosen for fulfilling both, the role of a solvent and a hydrogen donor instead of the gaseous hydrogen source. Performance of a capillary microreactor was tested for the model reaction and compared with literature data.

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In-situ UV-vis characterization of vanadium oxo species during C2-ODH reaction

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Abstract

Oxidative dehydrogenation of ethane (C2-ODH) represents an attractive and thermodynamically accessible route for the ethylene production. Vanadium based catalysts are one of the most studied and effective materials in this reaction. The nature of active and selective sites is still under discussion in particular ODH reactions. It is generally accepted that V-alumina catalysts possess high C2-ODH activity, while VO_x species supported on mesoporous silicas are characteristic by relatively high selectivity to ethane.

The contribution deals with the study of the distribution of vanadium oxide species distribution on mesoporous silica materials and alumina. Moreover, the attention is focused on the study of the redistribution of vanadium oxide species at both type of materials under presence of oxygen and reaction mixture (ethane, oxygen and helium).

Acknowledgement

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Properties of liquid products from catalytic biomass cracking

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Abstract

In this paper, some selected properties of treated liquid products (biooil) obtained from the cracking of biomass such as straw, saw dust and corn cobs are evaluated. Slow pyrolysis of biomass without the contact with oxygen is used for the biooil production at ambient pressure and temperatures up to 450 °C. As a catalyst, natural zeolite clinoptilolite is used. Properties of adjusted liquid products are evaluated for their use as alternative fuel for diesel engines. Two-stage biooil distillation is used for adjustment and correction of some biooil parameters as a density, viscosity, flash point, cetane index, distillation curve. Material balance of the process and the yield and composition of gaseous and liquid fractions are presented as well as the shares of cracking residues. An apparatus for biomass cracking and the process for the liquid fractions treatment are described.

Acknowledgement

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-0415-11 and by the program REACT (Programme AT-SK, European Union, European Regional Development Fund).

Mechanistic study of the reaction of glycerol and urea

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Abstract

By increasing demand of biodiesel a huge amount of glycerol is produced, because it represents 10% by weight of the product of the process. Glycerol can be turned into valuable product such as glycerol carbonate (GC). Both chemical and physical properties of GC are interesting for its utilisation as non-volatile organic solvent in coating materials, at manufacturing of medicines, cosmetics, polyurethanes, polycarbonates and many other useful materials. The main methods of preparation of GC are based on the reaction of glycerol with a carbonate source such as phosgene, dialkyl carbonate, urea, carbon monoxide and dioxide. By reaction of glycerol and urea under lowered pressure at mild temperatures - as in our study - yields and selectivities of glycerol carbonate around 80 % and 97 %, respectively, can be reached. Zn(II) catalysts seem to be the best for this process. Aim of our paper is to study the mechanism of the mentioned reaction. The reaction products, by-products and intermediates were proved by various analytical methods e.g. C^{13} NMR, H^1 NMR, FTIR, GC and, HPLC as well. In this work are also shown some possible ways for process failure as a result of overheating and reagent decomposition.

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Transformation of Glycerol to 1,2-Propanediol - Study of Reversible Reaction Steps

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Abstract

Recently the availability of glycerol as bio-diesel byproduct has inspired intense study of its different applications. The production of 1,2-propanediol (1,2-PD) is a relevant achievement of the new glycerol chemistry, which can replace fossil source with renewable one. Hydrogenolysis of glycerol to 1,2-PD is a two-step process. Glycerol is dehydrated to acetol in the first step and consequently, acetol is hydrogenated to 1,2-PD in the second step. Over many catalysts hydrogenolysis of glycerol can lead also to the formation of ethandiol. Catalysts based on copper, with addition of chromium and other transition metals, show good performance in these types of reactions. Direct hydrogenolysis of glycerol as well as hydrogenation of acetol and 1,2-PD were studied in a fixed-bed down-flow glass reactor with molecular hydrogen at mild conditions. Different temperatures, different flow rates of hydrogen, glycerol, acetol and 1,2-PD were studied and tested on copper-chromium catalysts supported on γ -alumina. Almost total conversions of glycerol and acetol and high selectivities to desired products were obtained. Because hydrogenation is a typical reversible reaction, the reversibility of all reaction steps was studied and the equilibrium composition of reaction mixtures was estimated at different condition.

Acknowledgement

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Ir (100) CO and O₂ induced reconstructions - a substrate material for model catalysts

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Abstract:

Many {100} surfaces of fcc metals like Ir, Au or Pt reconstruct and form a corrugated hexagonal surfaces. Thereby the hexagonal layer is lying in the hollow sites of the bulk substrate. This reconstruction of the surface is highly sensitive towards adsorbed species and can be altered upon adsorption of gases like CO, NO or O₂. By controlling the experimental parameters of the film preparation procedure we could prepare the (1x1) in a reducing environment, (5x1) reconstruction in an oxidizing environment and a (2x1) oxygen ad layer structure. All structural changes were followed by LEED.

The adsorption behavior of CO on each of the differently reconstructed surfaces was studied by LEED, PM-IRAS and TPD. The infrared results reveal an on top geometry over a wide pressure and temperature range.

The wavenumber of the C-O stretch vibration increases with increasing temperature on all three reconstructions. With increasing CO background pressure the wavenumber of the C-O stretch vibration increases steadily but then seems to converge towards a constant value on each surface reconstruction.

The CO TPD reveals three distinct desorption peaks for the (1x1) and the (2x1)-O structures and four peaks for the (5x1) reconstruction. Whereby in all three cases the low temperature species evolve with increasing surface coverage.

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In situ studies of CuNi/ZrO₂ catalysts: insights into surface modification processes during methane decomposition

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Abstract

Ni is applied as catalyst for methane reforming reactions, which are key processes for hydrogen production in industry and in solid oxide fuel cells. Ni shows high activity but is rapidly deactivated by coke formation, which is a major problem. The addition of Cu resulting in formation of a CuNi alloy is a potential means to reduce coke formation.

In this contribution we have characterized zirconia supported Ni and bimetallic CuNi catalysts and explored the formation of the CuNi alloy, the catalytic properties for methane decomposition and the surface composition in the reaction atmosphere to get insights into surface modification processes occurring as a consequence of the reaction with methane.

Characterization techniques used include TEM, FTIR spectroscopy, in situ XPS at mbar pressures, H₂ chemisorption and temperature programmed reaction. These methods provided information on Cu and Ni oxidation states, reduction temperature, catalytic performance, morphology and metal distribution on the surface. H₂ chemisorption indicated that the surface was enriched in Cu after reduction, in agreement with FTIR spectroscopy of CO adsorption. However, upon exposure to methane the concentration of metallic Ni at the surface strongly increased at around 673 K, as revealed by in situ XPS. This change in the surface composition of the bimetallic particles led to a sudden and irreversible increase in H₂ formation activity. In conclusion, the CuNi system behaves highly dynamic under reaction conditions, which limits the stability under reaction conditions.

Ni/silica based bimetallic catalysts by novel solid state co-reduction of admixed metal oxides for acetic acid hydroconversion to ethanol

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Abstract

Over monometallic catalysts (e.g. noble metals or Ni) hydrogenolysis is a characteristic reaction attacking C-C bonds. Hydrodecarbonylation may be the main reaction route hardly producing alcohols. Presence of indium atoms on the active metal surface (Ni or Pt) results in a drastic mechanism change moving to consecutive hydrogenation of carboxylic group resulting in selective formation of alcohols. Nickel and indium containing bimetallic catalysts can be easily formed with admixed In_2O_3 by the solid state co-reduction at 450 °C. The appearance of Ni_2In phases seemed to be responsible for the significant enhancement of the desired high activity and alcohol selectivity

The modification of the Ni particles with Sn, Cu or Ga following a novel co-reduction process of oxide forms also effectively directs hydrodeoxygenation of carboxylic acids to alcohols in consecutive steps and the presence of these metals hinders the chain shortening by hydrodecarbonylation of bioacids. This study reveals that In and Sn doped Ni/silica catalysts are outstandingly efficient bimetallic competitive composites. The lower reduction temperature of the In_2O_3 containing mixture is the main advantage of Ni_2In active phase formation used for alcohol production from fatty acids.

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Thanks is due to the Hungary-Slovakia Cross-border Co-operation Programme (Project registration number: HUSK/1101/1.2.1/0318) for supporting this research. Thanks to the European Union and the State of Hungary co-financed by the European Social Fund in the framework of TÁMOP 4.2.4. A/2-11-1-2012-0001 'National Excellence Program' for the further support.

Acetic acid hydroconversion to ethanol over supported nickel and indium modified nickel catalysts

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Abstract

Consecutive hydroconversion of acetic acid (AA) to ethanol was investigated over novel bimetallic catalyst (Ni₂In/SiO₂) varied the support (micro-, meso- and macro-porous, as well as amorphous or highly ordered amorphous) for the processing of volatile fatty acids that can be simply produced by biomass degradation. A fixed bed flow-through reactor was used with hydrogen flow at 21 bar total pressure in the temperature range of 220-370 °C. Over monometallic catalysts, hydrogenolysis is a characteristic reaction attacking C-C bonds. In such cases, hydrodecarbonylation may be the main reaction route hardly producing alcohols. Presence of indium atoms on the active metal surface results in a drastic mechanism change moving to consecutive hydrogenation of carboxylic group resulting finally in selective formation of alcohol. The textural properties of studied supports have a profound impact on the catalytic performance of Ni and Ni₂In active particles. Such bimetallic preparations are promising catalysts of the industry of fine chemicals.

Acknowledgement

Thanks is due to the Hungary-Slovakia Cross-border Co-operation Programme (Project registration number: HUSK/1101/1.2.1/0318) and to the European Union and the State of Hungary, co-financed by the European Social Fund in the framework of TÁMOP 4.2.4. A/2-11-1-2012-0001 ‘National Excellence Program’ for supporting this research.

Investigation of ^{14}C labeled oleic acid hydrotreating over different type of HDS catalysts

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Abstract

The conversion of oleic acid has been studied applying oleic acid labeled with radioactive carbon in carboxyl group (oleic acid-1- ^{14}C) to follow the hydrotreating process (reactions) of this compound over sulfided alumina-supported MoP and NiW catalysts. A flow-system catalytic reactor equipped with a special unit for microanalysis was applied for the study of the decarboxylation, decarbonylation and hydrodeoxygenation reactions at atmospheric pressure in the stream of hydrogen gas of different rates in the temperature range of 573-673 K. There were found only ^{14}CO , $^{14}\text{CO}_2$ and $^{14}\text{CH}_4$ among the gas products, and one of the alkanes ($\text{C}_{18}\text{H}_{38}$) was radioactive; only among those formed in the hydrodeoxygenation process. There were no radioactive products among the alkanes of carbon number < 18 . The ratio of ΣC_1 production was lower, and the energy barrier of that was higher, than the respective values, characterizing the production of $\text{C}_{18}\text{H}_{38}$. It is stated, that the sulfur leaves the ^{35}S -labeled sulfided catalyst samples at a very moderate manner, consequently the desulfurization of the samples at the conditions applied, can influence their catalytic activity only after a longer period. The radioactive microanalytical method based on the application of oleic acid-1- ^{14}C , is applicable well for the testing and evaluation of new catalyst samples in hydrotreating process of natural triglycerides.

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Dry reforming of methane on Ni, Pt and NiPt/ZrO₂ catalysts: preparation method versus catalytic activity in large excess of methane

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Abstract

Methane dry reforming ($\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2$) is of increasing importance regarding the sustainable energy management of our future. In this work two types of preparation methods were applied to get Ni, Pt and NiPt/ZrO₂ catalysts, and the differences in structure and catalytic behaviour measured in plug flow reactor with 70%CH₄+30%CO₂ mixture (to mimic biogas composition) were investigated and compared. The sample preparation was done by sol adsorption or impregnation. The calcined and reduced 1%Ni, 3%Ni, 1%Pt and the bimetallic 2%Ni1%Pt catalysts were characterized by XRD, TEM and HRTEM. The fresh catalysts contained nanoparticles in the range of 2-10 nm. Among Ni samples the impregnation, while for Pt samples the sol method yielded the best catalysts based on catalytic activities up to 600°C followed by a short 2h isotherm hold. The obtained CO/H₂>1 ratios suggest that at this relatively low reaction temperature, reverse water gas shift prevail to different extent depending on metal type and catalyst structure. The 24h stability measurements at 675°C revealed only 25% decrease in CH₄ conversion in the case of the best 3%Ni impregnated sample. Temperature programmed oxidation measurements showed that the amount of deposited carbon and the catalytic activity/stability are not in straightforward relation.

Acknowledgement

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The decomposition and production of dimethyl carbonate (DMC) on different carbon supported Cu, Ni and Cu-Ni catalysts

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Abstract

DMC can be a potential green chemical as an environmentally friendly compound. The decomposition of DMC was studied over solid acid and base samples [1]. Cu-based catalysts supported on activated carbon were found active in the oxidative carbonylation of methanol [2]. In this work the synthesis and the decomposition of DMC were investigated at atmospheric pressure on chloride free different carbon supported catalysts.

Carbon nanotube (MWCNT) and activated carbon (Norit) were impregnated with $\text{Cu}(\text{NO}_3)_2$ and $\text{Ni}(\text{NO}_3)_2$ solution to the yield 10 wt% metal content. The reactants and products were analyzed on-line by GC-MS.

In the decomposition the main products were CO_2 , dimethyl ether, methanol, methyl formate (MF) and dimethoxy methane. DMC was quite stable, it decomposed the easiest on Cu/Norit with 100 % conversion at 650 K, although it decomposed totally over the others even at higher temperatures ($\text{Cu/Norit} < \text{Ni/Norit} < \text{Cu-Ni/Norit} < \text{Ni/MWCNT} < \text{Cu/MWCNT} < \text{Cu-Ni/MWCNT}$). In case of the oxidative carbonylation of methanol the main products were CO_2 , MF and DMC. The yield of DMC formation was highest on Cu/Norit (13,2 %), it decreased in the order of $\text{Cu/Norit} < \text{Cu-Ni/Norit} < \text{Ni/Norit}$. On Cu/MWCNT the DMC yield was lower (1,2 %) but this sample was the most active among the MWCNT supported catalysts. From IR and XPS results it is obvious that the structure of the catalyst went through changes during the reaction. XPS showed the presence of Cu^{2+} and carboxylate groups on Cu/Norit that can mean that there is an interaction between Cu^{2+} and the oxygenated surface groups of activated carbon.

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Bimetallic Au-Cu/Al₂O₃ catalysts in oxidation of glucose and benzyl alcohol

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Abstract

The excellent properties of Au catalysts in selective partial oxidation processes performed with oxygen, which could be further improved by combination of Au with a second metal are demonstrated in the literature. In this work the structure-catalytic effect relationship is investigated in case of AuCu/Al₂O₃ in glucose and benzyl alcohol oxidation. Different structure AuCu nanoparticles were obtained by co- (Au&Cu) and subsequent reduction of Au- and Cu-precursors and vice versa (Cu→Au and Au→Cu, respectively) and stabilized in aqueous sol then adsorbed on alumina. The bimetallic catalysts and the monometallic analogous were characterized by high resolution transmission electron microscopy, UV-vis and X-ray photoelectron spectroscopy, CO chemisorption followed by FTIR and compared in glucose and benzyl alcohol oxidation after calcination and subsequent reduction. Alloyed AuCu and Au core–Cu-oxide shell type particles were formed in Au&Cu and Cu→Au samples, respectively, while in Au→Cu alloyed AuCu of less Cu-concentration than in Au&Cu was suggested with Cu-oxide decoration. The oxidative and reductive treatments induced some restructuring of the particles. Only the co-reduced AuCu/Al₂O₃ showed some synergetic activity increase in glucose oxidation; however its extent was much lower, than in the case of AuAg/SiO₂ (Ag/Au≤0.5) systems [1] studied earlier.

Acknowledgement

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Preparation of nanostructured TiO₂ using titanyl sulphate and extraction by pressurized and supercritical fluids

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Abstract

Since TiO₂ is widely used photocatalyst, titanyl sulphate is worldwide produced in tenths of tons per year and is economically perspective titanium source and processing by pressurized and supercritical fluids opens up the possibility to prepare nanostructured materials with different and improved textural and microstructural properties compared to those materials prepared by common thermal treatment, the preparation of TiO₂ by hydrolysis of titanyl sulphate solution and using the extraction techniques was studied. The effect of various extraction solvents (pressurized H₂O and pressurized/supercritical CH₃OH or CO₂) and conditions (*i.e.* temperature, pressure, volume and flow rate of extraction solvents, arrangement of extraction) on microstructure and purity of TiO₂ was investigated by means of nitrogen physisorption, X-ray diffraction, Raman spectroscopy and elementary organic analysis. The relationship between the type of processing and microstructure of synthesized TiO₂ was revealed.

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Preparation and characterization of Fe-doped TiO₂ thin layers

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Abstract

Fe-doped TiO₂ thin layers were prepared by the sol-gel technique controlled in the reverse micellar environment. Sol-gel Fe-doped TiO₂ layers were deposited on a substrate by the dip-coating method. For comparison the same techniques were used for preparation of pure TiO₂ layers.

The pure titania sol was prepared from nonionic surfactant (Triton X-102), cyclohexane, water and metal precursor (titanium isopropoxide, TIOP). For the Fe-TiO₂ preparation the iron solution was used instead of pure distilled water. As sources of iron iron (III) nitrate (Fe(NO₃)₃·9H₂O) and iron (II) sulphate (FeSO₄·7H₂O) were used. Then all types of prepared pure and Fe-doped TiO₂ layers were deposited on a substrate by the dip-coating method. To obtain the series of 1, 2, and 3 layers on a glass substrate the repeated dip-coating was applied by the laboratory dip-coater. The deposited sol on substrates were dried on air and then the organic matter was removed by calcination. The calcination was carried out at 450 °C for four hours to obtain the crystalline structure of pure anatase and mixed phase of hematite/anatase. The structural properties of the prepared layers were characterized by series of methods involving Raman spectroscopy UV-Vis spectrophotometry and SEM.

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Preparation and characterization of highly photoactive TiO₂ foam

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Abstract

Titanium dioxide is the most frequently used photocatalyst in the last decade. There are several different methods for the preparation of such photocatalyst. Our group deals with the preparation of TiO₂ foam from an aqueous solution of titanylsulphate.

In the first step, titanylsulphate was dissolved in distilled water and the solution was precipitated by ammonia solution to reach pH 8. The white precipitate was filtered and washed to remove SO₄²⁻ formed in the reaction. Then the pH value was reduced by H₂O₂. The resulting colloidal solution was lyophilized, and subsequently annealed.

The synthesized samples were studied by X-ray diffraction, electron microscopy, and the specific surface area was determined by the B.E.T. method. The photocatalytic activity was characterized using 4-chlorophenol in an aqueous solution as a model compound.

The lyophilized samples are amorphous. Annealing at 500 °C results in the formation of anatase crystalline structure. Further increase in annealing temperature to 950 °C means an increase of size of crystallites from 30 to 150 nm and decrease in the value of specific surface area from 11 to 35 m²·g⁻¹.

It was shown that by this method it is possible to prepare highly photoactive materials with photocatalytic activity better (1.5x) than P25 (Evonik-Degussa) often considered as so far the most active commercial photocatalyst. In the next step, we would like to dope samples to shift light absorption to the visible range of solar spectrum and utilize higher fraction of solar light.

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Electrophotocatalytic disinfection of water by interdigital electrochemical cells

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Abstract

Planar, interdigital photoelectrochemical cells were made by a combination of subtractive and additive procedures. First, a TCO base electrode pattern (F:SnO₂) needed to be fabricated by printing a negative UV curable polymer mask on FTO covered glass plates. Unprotected FTO was removed by the usual etching in HCl and zinc. After etching, the mask was removed by burning in a furnace at 450 °C, revealing the base electrode pattern. The electrode fingers had widths from 200 to 1500 µm. On one finger family, a previously developed TiO₂ sol was printed, using several passes, followed by gelling and annealing in air, which led to 10 to 240 nm thick TiO₂ deposits. The interdigital geometry ensured that the photoelectrochemical response of the printed cells was not suffering from iR drop down to low electrolyte ionic strengths. The best performing electrode designs were then used for water disinfection study with model microorganism *E. coli* at different concentration. A number of surviving bacteria cells was evaluated by a plate count method.

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WO₃ thin films prepared by pulsed plasma and particle deposition

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Abstract

Tungsten oxide is an important material with electrical and optical properties that are exploited for a variety of applications such as photolysis, electrochromic devices and gas sensors. Tungsten trioxide (WO₃) is an indirect bandgap semiconductor with attractive electrical and optical properties. The present work deals with the comparison of photoelectrochemical properties of WO₃ layers prepared by particle deposition, magnetron sputtering deposition and their combination. The layers were prepared on FTO glass substrates (fluoride-doped tin oxide) and quartz. The particle deposition consists in applying the aqueous suspension of WO₃ particles (various concentrations) directly to the support's surface followed by drying and annealing at 450 °C. The magnetron sputtering deposition consists in using a high-power impulse magnetron sputtering (HiPIMS) system. Tungsten target was reactively sputtered in atmosphere of Ar + O₂ at constant gas pressure $p = 2.18$ Pa. Combined layers consist in particle layer covered by sputtered layer. XRD measurement and Raman spectroscopy showed that layers have monoclinic crystalline structure. Layers prepared by sputtering achieved higher photocurrents and were more stable than layers prepared by particle deposition sedimentation.

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Photo-electrochemical properties of WO₃ particulate layers

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Abstract

Tungsten trioxide is widely used for photocatalytic experiments, especially for those using visible light. It is indirect band gap semiconductor ($E_g \sim 2.5\text{--}2.8$ eV) that can capture approximately 12% of the solar spectrum and can absorb light in the visible spectrum up to 500 nm. It is also convenient material to be used for hydrogen production via photoelectrochemical water splitting. Layers formed by particles of material have advantage in relatively high specific surface area usable for the reactions. But the mechanical stability and conductivity of these layers are very low due to weak adhesion of the particles. Both can be improved by layer calcination. The aim of the present work was therefore the investigation of electrochemical properties of plain particulate WO₃ layers annealed at various temperatures.

Tungsten trioxide particle layers were prepared on FTO glass substrates by sedimentation of commercial WO₃ (99 %, Fluka) and further annealed at different temperatures to improve adhesion of WO₃ particles. Linear voltammetry of these layers was measured within periodically chopped light illumination. Different excitation lights were used: three with very narrow single peak at light spectra (315, 365 and 404 nm) and fourth at the standard solar illumination conditions (AM 1.5 G). Also the influence of the electrolyte/electrode (EE) and substrate/electrode (SE) illumination of layers was studied. Better adhesion at higher annealing temperatures results in more stable layers with higher photocurrent. Increasing of the annealing temperature above 500 °C caused the formation of undesirable crystal phases (produced by the reaction of WO₃ and FTO layer) and significant decrease in photocurrent.

Key parameters of semiconductor layers for photoelectrochemical water splitting application are maximum photocurrent and the stability of the particle layers. It was experimentally proved that both can be significantly improved by thermal annealing at 450-500 °C. Using UVA or visible light is suitable for SE illumination of common FTO/ITO layered glass but for UVB light (<340 nm) illumination absorption spectra of the glass support must be considered.

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Efficient degradation of 4-chlorophenol with phthalocyanine complexes under sunlight conditions - comparison with laboratory data

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Abstract

The photochemical degradation of 4-chlorophenol was studied in the interaction with sunlight energy and phthalocyanine. Three different phthalocyanine was used – sulphonated zinc phthalocyanin, sulphonated aluminium phthalocyanine and citrate of sulphonated zinc phthalocyanine. The influence of different parameters e.g. concentrations of 4-chlorophenol, polychromatic and monochromatic light was studied. The obtained data was compared with laboratory data. The parameter of quantum yield was determined and used for mutual comparison of individual experiments. The photodegradation of 4-chlorophenol under the presented conditions appeared as an efficient degradation process. The presented process could be also used as a model process for the degradation of other organic pollutants.

Acknowledgement

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Semipilot waste water treatment by photocatalysis

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Abstract

In the recent several years, heterogeneous photocatalysis has evoked a great interest for the treatment of various types of organic contaminants found in wastewater or air. Endocrine disruptors (EDCs) presented at wastewater pose the real threat to the multicellular organisms. EDCs belong to the group of chemical substances disrupting the hormonal indication of vertebrates and thereby they could encroach on the organism function. To the group of endocrine disruptors belong surfactants, softeners, fungicides, insecticides and some kinds of medications and hormonal contraception. They are commonly presented not only in the waste water but also in the natural water. Unfortunately, conventional methods of water and sewage treatment are not completely effective in removing of the estrogenic substances. The necessity of finding the alternative solutions leads to development and use of the new technologies. Photo-catalysis using semiconductor particles have found increasing interest to solve the endocrine disruptors remove problems.

This study is focused on verification of the EDCs degradation by photocatalytical process in the specially designed pilot plant photo-reactor with immobilized TiO₂. The real waste water and the simultaneous water with 17- α -ethinyl estradiol and 4-nonylphenol as representative EDCs were tested. In this work the water decontamination with various concentrations of endocrine disruptors in the two types of reactors; batch and plug flow arrangement were also studied.

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Photo-electrochemical water splitting by TiO₂ thin film

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Abstract

The solar radiation on the Earth's surface represents a huge source of energy and its utilization and conversion to the useful form of energy has evoked a great interest in many industrial fields. The direct conversion of solar energy into hydrogen as energy carrier represents very encouraging application.

Hydrogen is one of the most promising candidates as a future energy carrier. The application that attracts a big attention today and potentially is more attractive route in hydrogen production is using the photo-electrochemical cells. This method is a very promising and environmentally friendly way for the water and sunlight conversion into hydrogen and oxygen. The photo-electrochemical water splitting involves the use of a photo-active semiconductor in water which after absorbing light with the corresponding energy is able to generate electron-hole pairs. The photo-excited electrons and holes are directly used to reduce and oxidize water, respectively. In an n-type semiconductor photo-anode, the electrons travel to the back contact and can pass to the counter electrode resulting in H₂ evolution.

Special attention of many researchers is focused on materials used as photo-anode since for the water splitting application the material properties play a crucial role. In this study the nanostructured TiO₂/FTO photo-anode was investigated. TiO₂ is the most extensively investigated material for photo-electrochemical application and possesses excellent stability over a wide range of pH values and applied potentials.

Acknowledgement

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Photocatalytic activity of self-cleaning paints during accelerated weathering tests in QUV panel

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Abstract

In addition of regular pigments and fillers, self-cleaning paints contain particles of photocatalytic material (anatase, ZnO) which acts as a sensitizer for photocatalytic processes. The self-cleaning ability of such paint is derived from a combination of photocatalytic activity and superhydrophilicity. The current commercial application of photocatalytic paints is mainly with regard to exterior facade paints which, via the photocatalytic process, are not susceptible to soiling and so help to keep the surface of the building clean. On the other side in the formulation of self-cleaning paint it is important to find compromise between photocatalytic activity and stability of the polymer binder with the respect to weather resistance.

Thus the objective of this work was to determine photocatalytic activity of several acrylic paints containing ZnO and TiO₂ photocatalyst exhibited to the accelerated weathering test. Photocatalytic activity was determined using smart inks. This method is based on irreversible colour change of dye in ink film on the photocatalytic surface. Ink containing reductive dye Resazurin (colour change from blue to pink) can be used for the most of paints. For the paints with high photocatalytic activity the colour change of resazurin is very quick. For such surfaces another ink containing dye Acid Violet 7 (the color change is from pink to colourless) can be applied.

Acknowledgement

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Photophysical and photochemical investigation of water-soluble, anionic gadolinium(III) porphyrins

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Abstract

Despite the important roles of metalloporphyrins in biochemistry, little is known about the consequences of the out-of-plane (OOP) or sitting-atop (SAT) coordination of the central atom. If it is not able to fit coplanar into the cavity of the ligand, because of its size and/or coordinative feature, it is located outside the plane of the porphyrin, deforming that. Due to this special coordination, an irreversible photoinduced charge-transfer from ligand to metal ion makes the charge separation more efficient. This feature allows the utilization of these complexes as catalysts in cyclic processes for synthesis of chemicals appropriate for conservation of light energy, e.g., in the cleavage of water, mainly by the use of lanthanide(III) porphyrins, as a consequence of the low redox potential of metal centers. In this work, we studied the formation and the primary photochemical features of the complexes of a water-soluble, anionic porphyrin and gadolinium(III) ion as the member of the lanthanide series with half-filled 4f subshell. The formation of complexes and the transformation between the mono- and bisporphyrins are very slow reactions in dark at room temperature. These reactions are accelerated by irradiation of the system; they are considerable by-processes of the photoredox degradation. We observed the formation of two types of photoproducts depending on the wavelength of photolysis.

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TiO₂ mediated photocatalytic mineralization of a nonionic detergent combined with other advanced oxidation procedures

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Abstract

Man-made surfactants in natural waters considerably hinder both the dissolution of atmospheric oxygen and the sedimentation of floating particles. TiO₂ mediated photocatalytic procedures proved to be a promising environmentally benign way to remove them. The efficiency of this method can be improved by combination of other advanced oxidation procedures such as ozonation.

Triton X-100 is one of the most widely applied man-made nonionic surfactants. This detergent (C₁₄H₂₂O(C₂H₄O)_n, consisting of a hydrophilic polyethylene oxide chain, on average $n=9.5$, and a hydrophobic aromatic hydrocarbon group) is utilized as both household and industrial cleaning agent. Since Triton X-100 can hardly be degraded by biological treatment, we have thoroughly examined its photocatalytic degradation under various circumstances (also combining with ozonation and treatment with peroxodisulfate). Mineralization of this surfactant was monitored by following the TOC and pH values as well as the absorption and emission spectra of the reaction mixture. An ultra-high-performance liquid chromatography (UHPLC) method has been developed and optimized for monitoring the degradation of the different components.

It has been established that Triton X-100 could be degraded by TiO₂ mediated heterogeneous photocatalysis, and its combination with other advanced oxidation procedures (AOPs) significantly enhances the mineralization rate.

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Photodegradation on [(1,10-phenanthroline-5,6-dion)-tetracyano ruthenate(II)] sensitized TiO₂

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Abstract

Semiconductor sensitization is an attractive approach for both conversion of light into electricity and photocatalytic hydrogen production as well as for the degradation of organic pollutants. Ruthenium(II) polyimine complexes compose the most investigated and efficient compounds of sensitizers. These complexes are usually bound to the surface of semiconductors with different ester groups, and there are only a few works where the binding group is a keto, hydroxyl or cyano group.

Here we present the photophysical and photochemical properties of [Ru(phendo)(CN)₄]²⁻ complex (phendo = 1,10-phenanthroline-5,6-dion)., which was applied as photosensitizer of TiO₂ for degradation of oxalic acid and phenylalanine as model compounds. The binding of this sensitizer on TiO₂ was optimum in acidic solution (below pH 3.5), where its efficiency exceeded 90 %.

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Bimetallic Ag-Au/SiO₂ catalysts in glucose and benzyl alcohol oxidations

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Abstract

Gold catalysts show high activity, selectivity and stability in liquid phase oxidation reactions. One way to improve the catalyst efficiency is the addition of a second metal to gold. The structure and activity of bimetallic silver-gold catalysts in selective glucose oxidation and benzyl alcohol oxidation was investigated. SiO₂ supported Ag-Au catalysts were prepared by sol adsorption method with 10/90, 20/80, 33/67, and 50/50 Ag/Au molar ratios. Reduction of HAuCl₄ in Ag sol resulted in alloyed Ag-Au colloid particles and that structures remained after calcination/reduction treatments. The Ag/Au surface atomic ratios were slightly higher than in the bulk. The effect of Ag addition to Au/SiO₂ resulted synergetic activity increase in glucose oxidation up to Ag/Au=33/67 molar ratio [1]. At Ag/Au=50/50 molar ratio no activity was detected as in the case of pure Ag/SiO₂. Catalyst stability was tested in glucose oxidation in a second reaction with the used calcined 10/90 Ag/Au molar ratio sample. The reaction rate of the used sample is decreased to 74 % of the fresh catalyst due to aggregation and metal leaching as was detected by HRTEM and UV-vis.

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Synthesis and characterization of novel Ru(II)-diimine complexes for combination of layered double hydroxides

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Abstract

Conversion of solar energy into chemical energy by using stable and efficient photosynthetic devices is a key and timely challenge. Molecular hydrogen, as a promising substitute for fossil fuels, makes the water splitting a prominently important catalytic process.

In the past decades the number of studies on the photochemistry of diimine-type Ru(II) complexes has extremely increased. These compounds can be dissolved in a variety of solvents by careful choice of the appropriate counter ion or ligand modifications. They also have a broad and intense metal-to-ligand-charge-transfer (MLCT) band in the visible region with a tunable maximum typically around 400 and 500 nm. The redox and excited-state properties can be tuned by the alteration of the ligands or ligand substituents. In practice, the bipyridine-type Ru(II) complexes as photosensitizers, can be a part of photocatalytic molecular devices. Moreover, using layered double hydroxides (LDHs) as substrate, a novel hybrid photosensitized system can be obtained.

Novel Ru-complexes with diimine ligands and their organic-inorganic nanohybrid forms are characterized by UV-visible spectroscopy, spectrofluorometry, secondary ion mass spectrometry (SIMS), fourier transform infrared spectroscopy (FT-IR). For the electroanalytical measurements, a potentiostat and cyclic voltammetry will be used.

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Heterogeneous catalytic hydroconversion of γ -valerolactone

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Abstract

Cellulose and hemicellulose are carbohydrate polymeric components of lignocellulosic materials. Hydrolysis of the polymer and acid catalyzed dehydration of the product hexoses provides levulinic acid (LA) with relatively high yield. The chemical industry looking for environmentally benign carbon source to produce biofuel, chemicals and other carbon-based products can use LA as platform compound. In consecutive hydrogenation and dehydration steps products like γ -valerolactone (GVL), 1,4-pentanediol (1,4-PD), and 2-methyltetrahydrofuran (2-MTHF) can be obtained. The GVL and the 2-MTHF are potential fuel additives and green solvents, whereas the 1,4-PD can be considered as polyester component. The selective conversion of the LA to a required useful product by heterogeneous catalytic process is a real challenge for the catalysis research. Catalyst can steer the attack of hydrogen on the GVL ring to get the required product. The C-O bonds in the GVL ring break the easiest giving either 1,4-PD or pentanoic acid. Depending on the reaction conditions the primary products of the GVL hydroconversion are further converted. For instance 1,4-PD can be further converted in dehydration hydrogenation reactions to different products, including 2-MTHF.

The present work concerns the GVL hydroconversion over Mo-containing Rh/SiO₂ catalyst, known as selective catalyst to form 1,4-PD. The activity of this catalyst was compared with those of our supported metal catalyst preparations.

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Steam reforming of methanol for hydrogen production over palladium supported on modified zinc oxide

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Abstract

Hydrogen is regarded as clean energy carrier. It can be produced from the range of fossil and bio-fuels using renewable energy sources, like wind, solar or geothermal energy, as well as through electrolysis by nuclear energy. Hydrogen for the mobile or portable systems can be obtained from methanol by the steam reforming reaction. Methanol reformers can be integrated in a single unit with high-temperature polymer electrolyte membrane fuel cell.

The aim of the studies was to develop palladium catalyst of high stability, activity and selectivity within the range 200–210°C for the reaction of the steam reforming of methanol.

A group of palladium catalysts was synthesized and studied by means of various physicochemical methods, including chemisorption of H₂, X-ray diffraction, X-ray fluorescence, transmission electron microscopy, temperature-programmed reduction. The steam reforming of methanol was carried out in a fix bed flow reactor under atmospheric pressure.

The results revealed high activity and stability of the catalysts. High selectivity to carbon dioxide and hydrogen was achieved.

Acknowledgement

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Catalyzed hydrogen oxidation in a nuclear power plant

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Abstract

Hydrogen generated during reaction of water with the Zircaloy fuel rods and pressure tubes in the nuclear power plants causes hydrogen embrittlement. Passive autocatalytic recombiners turn H_2 and O_2 into H_2O vapor to diminish the concentration of H_2 in air above a nuclear reactor. Usually, inside these devices are used supported Pt catalysts.

The most active catalysts in this reaction are expensive metals *i.e.* Pt and Pd. So we decided to propose the bimetallic catalysts combined with low-priced, nonprecious metals as nickel and cobalt. The Pd-Ni/ Al_2O_3 and Pt-Co/ SiO_2 catalysts were characterized with TPR, TPHD, chemisorption and their homogeneity was checked with XRD. The catalytic reaction was performed in the flowing system under atmospheric pressure with mixture 0.5% H_2 -air in the stream over an hour at room temperature. The process was carried out under diverse conditions: different flow and humidity of the reacting mixture. Before the proper reaction the catalysts were reduced in hydrogen and purged in helium. The course of the reaction was followed by mass spectrometer with electron multiplier. The determination method revealed high sensitivity for hydrogen and allowed continuous monitor the progress of reaction. At starting point almost all hydrogen had been converted to water but with lasting time a conversion was decreased asymptotically to presented values. The low-priced catalysts revealed a little lower activity than the high-priced, but their activity per active metal is promising. The lower concentration of precious metal was in the sample, the higher activity per this metal was observed. Low amounts of water in the reaction mixture decreases activity slightly but simple drying eliminates this effect.

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Physicochemical characteristics of metallic function of catalysts in reaction of hydrogenation of CO₂ in the way dimethyl ether

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Abstract

For a several years there has been observed expansion of interest in dimethyl ether (DME) as a potential fuel in diesel engines, heat and power stations, and fuel cells. The level of air pollution during combustion is lower than in case of combustion diesel oil. DME characterizes the low temperature spontaneous combustion what is connected with high its cetane number.

Hybrid catalysts are used to synthesis DME. They contain metallic functions (hydrogenation of CO₂) and acid constituent (dehydration of methanol).

Metallic function of hybrid catalyst CuO/ZrO₂ were obtained by different methods: co-precipitation with Na₂CO₃, co-precipitation with NaOH, and complexation with citric acid (citric method). These metallic functions were modified by Ga, Mn, Ag, Cr additives.

Specific surfaces areas of the metallic functions depend on the applied synthesis method. The metallic function obtained by co-precipitation with NaOH showed the highest surface area. On the other hand the lowest surface area showed those metallic functions which were obtained by co-precipitation with Na₂CO₃.

As comes out from the H₂-TPR measurements, the catalysts synthesized by various methods show different reduction profiles and reduction temperatures. The metallic functions obtained by the co-precipitation with NaOH method showed a single reduction peak, while preparations obtained by citrate method were characterized by double peak. In the case of the samples obtained by co-precipitation with Na₂CO₃ in TPR profile three peaks are visible. The catalysts CuO/ZrO₂ reduces between 180-360°C and the reduction temperature of catalysts with additives decrease. The greatest effect on initial reduction temperature was observed after silver addition. In the case that multiply peaks the low-temperature peak may result from small-size crystallites or weakly bonded with the surface of ZrO₂, whereas the high-temperature peak is involved with reduction of CuO crystallites which strongly interact with catalyst support.

TPR profiles and differences in the texture of these catalysts suggest that these modifications of the metallic functions may lead to changes of the catalytic properties.

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Mesoporous silica materials modified with organic titanium precursors – FT-IR studies

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Abstract

Mesoporous materials are of great interest to the materials community because their pore structures as well as catalytic, adsorbent, conductive and magnetic properties can readily be tailored. Incorporation of transition-metal ions into the frameworks of the molecular sieves is a general method for introducing catalytic sites into mesoporous materials. TiO_2 has been considered as one of the most promising photocatalysts because of its nontoxicity, photo- and chemical- stability, low cost, and superior photocatalytic activity. The titanium-functionalized SBA-15 material has recently received much attention because of its superior mechanical and chemical resistance compared with other mesostructured materials. For this purpose different synthetic pathways can be employed, being the post-synthetic methodologies and the direct synthesis protocols the most widespread alternatives, though the latter option displays several advantages like the higher dispersion degree and stability of the final metallic sites. However, it is very difficult to incorporate titanium into silicate framework under acidic medium by using amphiphilic tri-block copolymer as template through co-condensation of silicon and titanium alkoxide precursors due to different rate of hydrolysis of both alkoxide precursors. Incorporation of titanium into silicate framework in the presence of amphiphilic tri-block copolymer through a grafting method under aqueous acidic medium has been reported.

Therefore the synthesis of catalytically active Ti-SBA-15 still remains a big challenge and in this work will be presented the results of the titanium ions introduction on the surface of SBA-15 materials.

Lanthanum oxide modified pre-reforming nickel catalyst

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Abstract

To start-up the LNG (Liquefied Natural Gas) terminal in Świnoujście (north-west Poland) contribute to the increase of Polish energy security. The conducted project is to indicate the possible effects of LNG application in nitrogen industry. To eliminate the risks as a consequence of the presence of higher hydrocarbons in the feedstock there should be provided to supplement working installation of pre-reforming process over a new catalyst.

Presented poster shows the effect of the addition of small amounts of La_2O_3 on physico-chemical properties, activity, thermal stability and resistance to coking of high nickel loaded catalyst. There was examined the influence of catalysts annealing at 600, 700 and 800°C (simulating long-term operation) on the development of the total surface area, nickel dispersion and the sintering resistance, as well as the activity and the resistance to coking in the steam reforming reaction of hydrocarbons. Obtained results indicate that the presence of La_2O_3 causes improvement of physico-chemical properties and the resistance increase for sintering and coking of the nickel catalysts used.

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Vibrational Sum Frequency Generation Spectroscopy on Catalysts Surface

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Abstract

Vibrational Sum Frequency Generation Spectroscopy (V-SFG) is a surface characterization technique applying a non-linear second order optical phenomenon. It allows to measure vibrational spectra at surfaces and interfaces of adsorbed and reacting molecules without any contributions from gas-phase molecules and bulk. V-SFG is accessible to all kind of surfaces gas-liquid, liquid-liquid, and liquid-solid, gas-solid and solid-solid.

Advantageous is the broad pressure level range starting from atmospheric pressure to ultra-high vacuum conditions.

Since the generation of the sum frequency process delivers low signal intensities, picosecond lasers are in use.

A tunable IR radiation induces the transition from the ground state to an excited state. The visible laser is responsible for the transition to higher energy virtual state through an anti-Stokes Raman process. Both lasers have to overlap temporally and spatially on the surface.

Our work will focus on catalytic, thin film surfaces. Interesting are metal nanoparticles such as Pt, Pd supported by thin oxide films (ZrO₂) grown on single crystal substrates, adsorbates structure.

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Synthesis and examination of palladium supported zinc-aluminum oxides catalysts for methanol steam reforming

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Abstract

Currently a great attention is paid to the environmental problems and the modern technology of energy generation. One of the solutions is environmental friendly production of electricity with the use of hydrogen-based fuel cells (PEMFC). The main disadvantage of the PEMFC technology is hydrogen storage and distribution. This technical problems could be overcome by production of hydrogen in small installations or on the board of vehicles, using steam reforming of methanol. Recent research studies are focuses on obtaining highly stable, selective and active catalysts. Microemulsion method has aroused a lot of interest for catalysts preparation. This method enables in easy way to control the reversed micelles, and thereby the particle size or shape by changing the water-to-surfactant molar ratio (W_0). The microemulsion method might be used for preparation of materials with a suitable chemical composition and distribution of the species with control on nanometer level, different porosity or specific surface area.

Palladium supported zinc-alumina oxide catalysts were prepared by microemulsion method. The aim of the studies was determination of the influence of W_0 on the properties of catalysts. The physicochemical properties of catalysts were characterized by nitrogen adsorption-desorption method, X-ray diffraction and X-ray fluorescence methods. Surface properties of the catalysts were studied by means of carbon monoxide adsorption and desorption of methanol using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). High Resolution Electron microscopy was used to determine the shape and size of the crystallites. The obtained catalysts exhibited different structural and surface properties and activity in methanol steam reforming reaction.

The carbonylative Suzuki cross-coupling reaction catalyzed by H – spirophosphorane palladium complexes

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Abstract

In the last decades the carbonylative cross-coupling reactions of arylboronic acid with aryl halides are significant interest in academia and fine chemical industry. Nowadays, varieties of palladium catalysts are available for the synthesis of symmetrical and unsymmetrical ketones or aldehydes, which are important intermediates in manufacture of pharmaceuticals, agrochemicals and other industrial product.

Until now, catalytic activity of palladium complexes incorporating hydrospirophosphorane ligands in carbonylative Suzuki reactions of arylboronic acid with aryl halides have been never studied. In this work the coordination properties of $\text{HP}(\text{OCH}_2\text{CH}_2\text{NH})_2$ and $\text{HP}(\text{OC}_6\text{H}_4\text{NH})(\text{OCMe}_2\text{CMe}_2\text{O})$ ligands towards $[\text{PdCl}_2(\text{cod})]$ and $[\text{Pd}(\mu\text{-Cl})(\text{C}_3\text{H}_5)]_2$ precursors has been performed. Four catalysts $[\text{PdCl}(\text{C}_3\text{H}_5)\{\text{P}(\text{OCMe}_2\text{CMe}_2\text{O})\text{OC}_6\text{H}_4\text{NH}_2\}]$, $[\text{PdCl}_2\{\text{P}(\text{OCH}_2\text{CH}_2\text{NH})\text{OCH}_2\text{CH}_2\text{NH}_2\}]$, $[\text{PdCl}_2\{\text{P}(\text{OCMe}_2\text{CMe}_2\text{O})\text{OC}_6\text{H}_4\text{NH}_2\}]$, $[\text{PdCl}(\text{C}_3\text{H}_5)\{\text{P}(\text{OCH}_2\text{CH}_2\text{NH})\text{OCH}_2\text{CH}_2\text{NH}_2\}]$ with hydrospirophosphorane ligand connected to palladium atom in bidentate mode have been obtained and characterized by spectroscopic methods. The catalytic activity of these catalysts was tested in carbonylative Suzuki reaction of phenylboronic acid with 4-iodoanisole. Results show that under mild reaction conditions (2h, CO (balloon pressure), 100 °C) these complexes are relatively high-yielding and selective catalysts for Suzuki carbonylative cross-coupling reaction. Analysis of post-catalytic solution by using Transmission Electron Microscopy showed the presence of palladium nanoparticles which are generated *in situ* during reaction.

MgO-RX catalytic systems for chemoselective transfer hydrogenation of acrolein with ethanol

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Abstract

New catalytic systems were prepared by chemical vapor deposition (CVD) of various alkyl halides onto the surface of MgO. It was found that the reactivity of RX in the reaction with MgO increases with the order of the alkyl halide: primary < secondary < tertiary. For *t*-BuX (X = Cl, Br and I) the following order of their reactivities was found: *t*-BuI < *t*-BuBr < *t*-BuCl. It was shown that after treatment of MgO with these compounds, the concentrations of halide anions incorporated into MgO ranged from 0.1 to 19.3 mmol/g. The resulted systems were characterized by nitrogen physisorption (S_{BET}), chemical analysis (amount of X⁻) and XRD measurements. The strength of acidic and basic sites on the surface of MgO-RX systems was determined using Hammett's indicators. The concentration of these sites was measured by titration with solutions of *n*-BuNH₂, Et₃N and PhCO₂H in toluene, and also by using TPD of acetonitrile and pivalonitrile.

The interaction of MgO with RX vapors causes a strong decrease of the strength and concentration of basic sites of the oxide with a simultaneous appearance of Brönsted-type acidic sites of a modest strength.

The activity of the prepared catalytic systems in vapor phase transfer hydrogenation of acrolein with ethanol was studied. At 473 K, a 65% yield of allyl alcohol was attained (chemoselectivity 97%) in the presence of MgO-MeI, in comparison to 15% (chemoselectivity 100%) in the presence of pure MgO.

Transfer hydrogenation of various ketoesters with alcohols in the presence of magnesium oxide

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Abstract

Two series of ketoesters: a) $\text{CH}_3\text{CO}(\text{CH}_2)_n\text{COOR}$ ($n = 0, 1, 2$ and 4 ; $R = \text{Et}, i\text{-Pr}$ and 2-octyl) and b) $\text{PhCO}(\text{CH}_2)_m\text{COOR}$ ($m = 0$ and 2 ; $R = \text{Et}, i\text{-Pr}$ and 2-octyl) were used as hydrogen acceptors from secondary alcohols $\text{CH}_3\text{CH}(\text{OH})\text{R}'$ ($\text{R}' = \text{Me}, \text{Et}, n\text{-Pr}$ and $n\text{-C}_6\text{H}_{13}$) under normal pressure in liquid-phase in the presence of MgO as a catalyst. No reaction was observed with aliphatic α - and β -ketoesters due to an immediate deactivation of the catalyst caused by acidic properties of the ketoesters. For other ketoesters it was found that the transalcoholysis reaction of the starting ketoester with a hydrogen donor is much faster than its transfer hydrogenation, e.g. for 2-octanol and 2-propyl 6-oxoheptanoate (ϵ -ketoester) a 61% yield of 2-octyl 6-oxoheptanoate and a 35% yield of 2-octyl 6-hydroxoheptanoate, respectively, were observed after 6 h. It was shown that for transfer hydrogenation of a γ -ketoester, such as 2-propyl levulinate, the primary product (hydroxoester) is unstable and undergoes cyclization to γ -valerolactone. By changing the hydrogen donor from 2-propanol to 2-nonanol and increasing the reaction temperature from 355 to 467 K, we were able to increase the yield of γ -valerolactone from 2 to 52% after 6 h.

In the second series of ketoesters, which contain phenyl as a substituent, ethyl benzoylformate in the presence of MgO was hydrogenated with 2-octanol to ethyl mandelate (4%) and 2-octyl mandelate (50%). A 45% yield of 2-octyl benzoylformate was also observed after 6 h of reaction. For the transfer hydrogenation of 2-propyl benzoylpropionate (γ -ketoester) with 2-octanol a 64% yield of 5-phenyl- γ -valerolactone as a sole product was noted after 6 h of reaction.

DFT modeling of tungsten heteropolyacids modified by Cu ion(s).

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Abstract

In this paper tungsten heteropolyacids (HPA), modified by copper ions, are presented. We compare the electronic structure of HPA with different geometric structure: systems with Keggin geometry (build by central tetrahedron PO_4 surrounded by 12 edge- and corner-sharing metal-oxygen octahedral) in which Cu^{2+} cation was introduced in the position of central ion, $\text{CuW}_{12}\text{O}_{40}^{6-}$ (CuW) or in the position of one of the addenda atom, $\text{PW}_{11}\text{CuO}_{39}^{5-}$ (PWCu); systems with Dawson geometry (build by two trivacant Keggin anion connected by six edges) $\text{PW}_{17}\text{CuO}_{61}^{n-}$ ((PW)₂Cu) where Cu ions occupies different position as addenda atoms as well as the sandwich type heteropolyacids where Cu cluster is localized between two trivacant heteropolytungstate Keggin anion. Electronic structure of modified Cu-HPA were carried out within the DFT approach with cluster model using Turbomole code. The effect of solvation by water was taken into account within COSMO approximation. The results of calculations for modified Cu-HPA show that changes in chemical composition lead to the changes in physicochemical properties of the studied system. The analysis of character of frontier orbitals and spectrum of density of states suggests that in modified system the reduction process will occur with participation of copper ion. We will discuss the impact of the geometric environment on the properties of Cu ions.

Acknowledgement

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Modification of Keggin anion by cations from first row transition metal.

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Abstract

The structure of HPA allows for numerous modifications through substitution of various elements such as central ion, addenda atoms and compensating cations. In this work calculations for two groups of modified tungsten and molybdenum Keggin anions were performed, systems where one addenda atom (Mo/W) was replaced by transition metal cation. The first group contains systems with general formula $H_nPW_{11}(Mo_{11})TMO_{40}$ where $TM = Ti^{4+}, V^{5+}$ whereas the second group define systems with general formula $H_nPW_{11}(Mo_{11})TMO_{39}$ where $TM = Cr^{3+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}$.

The impact of the addenda atom on properties of modified systems was studied carrying out the DFT calculations (package Turbomole) using cluster model. Optimized geometries, densities of states, various population analyses, as well as the character and energy of boundary orbitals were determined. Additionally Natural Orbital Chemical Valence method was used to investigate the role of introduced addenda atom on the activation process of small molecules (O_2 , OOH^*) in terms of quality and quantity.

For all studied cases calculated density of states spectra show that the valence band close to the Fermi level is dominated by $2p$ orbitals of the oxygen bridging centers. On contrary the conduction band comes mainly from the d orbitals of addenda metal cations, in particular, from the introduced new one. In addition, the chemical character of the introduced addenda atoms determines the energy levels of frontier orbitals and the size of band gap. Moreover, the size of band gap is a reflection of the reduction abilities of the systems; according to the NOCV analysis the activation process of small molecules is dependent on the nature of transition metal introduced into the Keggin framework.

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Modification of cobalt sites in zeolites by coadsorption of electron donor/acceptor ligands and its impact on the strength of NO bond

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Abstract

Coadsorption of small molecules is the way to change the catalytic activity of transition metal sites in porous materials. In this theoretical study the cation Co^{2+} is embedded in the simplest fragment of zeolitic framework, comprising a single aluminium and four oxygen ions saturated by hydrogen what can be written as $[\text{Al}(\text{OH})_4]^-$. Our investigation concerns the range of NO activation or deactivation caused by interacting with the cobalt site in the presence of CO or NH_3 coligands. To this end, we use the SR-NOCV (spin resolved natural orbitals for chemical valence) method to scrutinize the electron density flow accompanying the bond formation between well-defined fragments of the complex. The analysis is based on the DFT:BP86 approach. Moreover, the research is supported by more advanced calculations at CASSCF/CASPT2 level, enabling us to discuss the relative energy of spin states. Additionally, we propose the description of the Co-NO bond in terms of covalent and donor-acceptor character. Properties of NO are strongly dependent on the kind of electron ability of molecule(s) coadsorbed on the cobalt site. Interestingly, the obtained result may be different for close lying singlet and triplet states of the adduct found in our study. The general tendency is that electron acceptor CO leads to strengthening of the NO bond while electron donor NH_3 weakens it. This is evidenced by observed blue- and red-shift of NO stretching frequency in comparison to free molecule, respectively. Moreover, this indicates the competition for electrons between coadsorbed ligands.

Acknowledgement

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Steam reforming of glycerol over Ni/Al₂O₃ catalysts modified with ceria or/and zirconia oxides

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Abstract

High growth of fossil fuels prices and tighten environmental requirements, which restricts emissions of the contaminants released to the atmosphere, affecting on increase of the share of energy possessed from renewable sources, including biomass. One of the most popular ways of processing vegetable oils is their transesterification, which lead to obtaining so called biodiesel. This process gives, beside the main product, technological waste, which is glycerol fraction. This waste contains up to 80% of glycerol and constitute average ~10 wt. % of produced esters. Only in 2012 world biodiesel production was approximately ~27 mln tons. This means ~2,7 mln tons of waste glycerol. Beside already known applications of glycerol in pharmaceutical, food, cosmetics and tobacco industry or explosives materials, many research groups began to propose new processes having their purposes in fitting up this waste. One of the promising processes seems to be steam reforming of glycerol to synthesis gases. Through this reaction high amounts of hydrogen can be obtained, on which is still growing demand (i.e. for hydrogen fuel cells).

The aim of this work was to study the steam reforming of glycerol reaction using Ni catalysts prepared by two different methods and selecting optimal conditions for hydrogen production. First series consist four Ni catalysts impregnated on alumina oxide modified by ceria or/and zirconia oxides. Second series consist nine Ni catalysts with active phase modified by ceria or/and zirconia oxides. All tests were performed under atmospheric pressure at 650-800°C temperature range using glycerol:water mixture (S/C = 3). Also all catalysts have been well characterized by physiochemical methods (XRD, XRF, TPR). The results were shown as glycerol conversion, hydrogen and carbon products (CO, CO₂, CH₄ and C₂H₄) selectivity.

An application of carbon materials for synthesis of zinc oxide by nanocasting method

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Abstract

Zinc oxide has been widely used in rubber industry, production of ceramic, pigments, concrete, coatings and cosmetics. ZnO shows the unique electronic and optical properties, and can be used for preparation of new materials for cutting edge technologies, e.g. light-emitting and laser diodes, varistors, gas sensors, magnetic materials, photocatalysts. ZnO is also a component of numerous industrial catalysts and adsorbents, e.g. for low temperature water gas shift reaction (WGS), methanol synthesis, desulfurization. Recent studies carried out within the research project entitled “Development of an Internal Reforming Alcohol High Temperature PEM Fuel Cell Stack (IRAFC)” revealed that the activity, selectivity and stability of palladium catalysts in the reaction of the steam reforming of methanol were partially related to the properties of zinc oxide support.

The main goal of the current studies was to investigate the effects of the different synthesis conditions on the structural and surface properties of zinc oxide support for palladium catalysts. Zinc oxide was prepared by means of novel nanocasting method using carbon materials as hard-templates. It was stated that the structural properties and morphology of ZnO can be tailored by the suitable choice of the type of carbon materials, gasification temperature during template removal and gas phase composition. The dilution of oxygen with an inert gas or decrease of the treatment temperature allows formation of ZnO with high specific surface area, which is composed from the small crystallites, shaped in the flower-like morphology.

Acid sites in MFI type zeolite isomorphously substituted with boron

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Abstract

Brønsted active sites in zeolites are generated as a result of isomorphous substitution of tetravalent Si^{4+} cation in the SiO_4 tetrahedra by trivalent cations (for example Al^{3+} , Fe^{3+} , B^{3+}). The strength of the Brønsted acid site depends on the nature of the cation substituting Si^{4+} . Boron containing zeolites are characterized by the presence of weaker acid sites than their aluminum counterparts. Low thermal stability of acid sites in B containing molecular sieves leads to extraction of boron from the framework during a high temperature treatment and formation of so-called internal silanol groups $(\text{Si-OH})_{\text{int}}$ with similar acidic strength to Brønsted acid sites related with framework boron (Si-OH-B) .

The aim of this paper is clarification which of the above centers are responsible for the acidic properties of borosilicates. Both types of samples (B-MFI zeolites) were prepared by using different conditions of post-synthesis treatment (ion-exchange with NH_4NO_3 or H_3BO_3 and activation at 450 and 250 °C respectively). Attempt to distinct the two types of active sites was carried out by means IR spectroscopy (pyridine adsorption).

Significantly higher intensity of 1550 cm^{-1} band observed in the spectrum of the sample exchanged with NH_4NO_3 and after activation, indicated much higher number of weak acid proton sites in this sample. This is probably the effect of removal of B^{3+} ions from framework at 450°C and formation of internal silanol groups $(\text{Si-OH})_{\text{int}}$ - one Si-OH-B group replaced by 4 $(\text{Si-OH})_{\text{int}}$ groups).

The band at 1550 cm^{-1} (PyH^+) is much weaker in the case of the sample after ion-exchange with boric acid. Additionally the intensive band (1445 cm^{-1}) associated with aprotonic Lewis sites is present as a result of low ion exchange degree (pyridine chemisorbed on the sodium cations). The band at 1460 cm^{-1} indicating the presence of stronger Lewis-type acid sites (more intensive in the case of B-MFI_{H₃BO₃,250}), is probably associated with the presence of trigonal boron in lattice (B-MFI_{H₃BO₃,250}) or/and extra-framework boron (B-MFI_{NH₄NO₃,450}).

Preliminary results obtained above turn out not fully conclusive and suggested that the samples treated with boric acid require repetition of ion-exchange process in order to increase H^+/Na^+ ratio. To improve the results and complete analysis, spectroscopic studies on the nature of non-framework centers present in the tested materials as well as catalytic test of the both types of samples will be done.

Acknowledgement

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Turbostratic carbon supported Ni-Pd alloys in aqueous-phase hydrodechlorination of chloroorganic compounds

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Abstract

The continuous development of industry results in significant water pollution by very toxic substances such as chloroorganic compounds. Chlorinated hydrocarbons are particularly dangerous due to their potential carcinogenic and mutagenic effects. The aim of this study was to investigate the effect of addition of palladium on catalytic behavior of turbostratic carbon supported nickel catalyst in aqueous-phase hydrodechlorination of trichloroethene (TCE) and tetrachloroethane (TeCA). Catalytic tests were performed at mild operating conditions (303 K, 1 atm, 1000 rpm) in a round bottomed flask, using 350 mL MiliPore water and 2.0 µL of TCE or 1.9 µL of TeCA. The substrate concentration was monitored using a Bruker gas chromatographic system equipped with ECD and FID detectors. The combination of turbostratic active carbon and very well mixed Ni-Pd alloys gave active catalysts in hydrodechlorination of TCE and TeCA in liquid phase without presence of organic solvent in the reaction mixture. Synergy in the catalytic behavior of Ni-Pd alloys is attributed to modification of electronic structures of Ni and Pd upon alloying (electronic/ligand effect).

Acknowledgement

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Mesoporous silicas modified with Keggin oligocations as effective catalysts for synthesis of DME from methanol

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Abstract

The problems concerning energy, such as depletion of fossil fuels or pollution of the environment, had been of much interest during last years. The alternative fuel, which can address several of those problems could be dimethyl ether (DME). It can be used as a diesel substitute, due to its high cetane number and similar physical properties to diesel fuel. DME synthesis from alcohol is acid-catalyzed, exothermic reaction, that is carried out in the temperature range of 250-400°C and at pressures up to 18 bars. Catalysts with strong acid sites produce light olefins as a main product and promote coke formation, while catalysts with medium and weak acid sites convert methanol mostly to dimethyl ether. Thus, surface acidity seems to be a crucial parameter determining the properties of the catalysts for DME production.

The presented studies are focused on development of active, selective and stable catalysts for synthesis of DME from methanol. Mesoporous silica sieves of type SBA-15 and MCF modified with alumina Keggin oligocations (Al13) were tested in the role of catalysts. The procedure of oligocations deposition consisted of the following steps (i) grafting of thiol groups (-SH) by postsynthesis reaction of mesoporous silicas with (3-mercaptopropyl) trimethoxysilane (MPTMS); (ii) oxidation of -SH groups to -SO₃H using H₂O₂; (iii) deposition of Al13 cations by ion-exchange method; (iv) calcination of the samples. For comparison also the samples obtained by impregnation of Al13 cations were tested. Moreover, oligocations containing copper (Al12Cu1) and iron (Al12Fe1) were introduced into the silica SBA-15 and MCF supports. The obtained samples were found to be active, selective and stable catalysts for the process of DME. The most promising results were obtained for the mesoporous samples modified with transition metal containing oligocations.

Effect of cesium doping on the deN₂O activity of cobalt spinel

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Abstract

Metal oxides with spinel structure are widely investigated as catalysts for low temperature N₂O decomposition. Co₃O₄ was found to be one of the most active materials. Our previous studies revealed a strong promotional effect of K, manifested by shifting of deN₂O reaction temperature window by 160°C upon optimized K doping of Co₃O₄. This effect, which appears within a narrow potassium surface coverage, was explained in terms of electronic promotion of the catalyst, gauged by lowering of its work function. In this communication the effect of cesium on cobalt spinel deN₂O performance, was examined to determine the strength of electronic promotion and an optimal precursor nature and loading. A series of Cs-Co₃O₄ samples were prepared by incipient wetness impregnation of cobalt spinel ($S_{\text{BET}} = 60 \text{ m}^2/\text{g}$), with different cesium precursors: Cs₂CO₃, CsNO₃, CsOH and CH₃COOCs (Cs loading in the range of 1-10 atoms/nm²). After drying at 100°C for 1 h, the samples were calcined at 500°C for 4 h. The catalysts were characterized by means of RS, XRF. The electronic properties were investigated by work function measurements (Kelvin method). The catalytic activity of N₂O decomposition was studied in quartz flow reactor, using 0.3 g sample as a sieve fraction between 0.2 – 0.3 mm with a flow rate 30 ml/min 5% N₂O in He and heating rate 10 °C/min from 50 to 600°C. Strong correlation between the catalytic activity ($T_{50\%}$) of N₂O decomposition and the work function was observed for the series of the catalysts prepared by impregnation with carbonates, hydroxides and acetates, confirming the electronic nature of cesium promotion of Co₃O₄. In each case the strongest promotional effect was obtained for cesium loading at the level of 2-3 atoms/nm². The highest decrease of work function ($\Delta\Phi = 0.5\text{eV}$) obtained upon doping of cobalt spinel with Cs₂CO₃ corresponds to the highest increase of the catalytic deN₂O activity ($\Delta T_{50\%} = 260^\circ\text{C}$), much higher than for K-doping.

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Catalytic activity of nanooxides obtained via continuous flow synthesis in supercritical conditions

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Abstract

Development of new generations of catalysts and other materials based on oxide structures (e.g. sensors) depends on our ability to control size, shape and surface chemistry of constituent elements. Supercritical fluids (SCFs) have been proposed as media to produce nanomaterials. The properties that make supercritical fluids particularly attractive, as a rule, are gas-like diffusivities, the continuously tunable solvent power/selectivity and the possibility of complete elimination at the end of the process. The vast majority of inorganic hydrothermal syntheses tend to be conducted in batch reactions, which can be time-consuming and give little or no control over particle properties or phase composition. In the continuous operation, metal salt aqueous solution is mixed with high temperature water fed from another line, thus providing a high nucleation rate obtained when the supercritical solvent is mixed with cold reactant. This method enables for the continuous and rapid production of nanocrystals with well-defined and narrow size distribution.

The developed continuous supercritical method procedures were used for the synthesis of the series of nanooxides. The model oxide nanomaterials were chosen on the basis of their possible catalytic application. These include: Co_3O_4 , Fe_2O_3 , Fe_3O_4 , CeO_2 . Depending on the reaction conditions: pressure, temperature, residence time in the reactor and substrates concentration crystals of different size and shape were obtained. The obtained powder materials were characterized with respect to their physicochemical properties with the emphasis put on the structure and surface reactivity. Catalytic properties of the obtained materials were tested in the N_2O decomposition and soot oxidation reactions.

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Preparation and characterization of a ceria-zirconia catalyst for DMC synthesis

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Abstract

Number of methods have been reported in the literature for the preparation of dimethyl carbonate (DMC) as an important chemical compounds typically applied in methylation and carbonylation reactions. Recently a particular attention has been paid to the reaction of methanol with carbon dioxide as an alternative to other syntheses involving hazardous and toxic components [1]. In such a reaction system a highly active catalyst is required to make this method competitive in comparison with other types of synthesis routes.

In this work we report on the preparation of ceria-zirconia mixed-oxides, which are considered as particularly promising for meeting the requirements leading to performable DMC synthesis. The synthesis strategy is based on the preparation of a supported catalyst starting from polymeric sols/gels (prepared by the Pechini method) which are subsequently deposited/infiltrated uniformly on/in inert porous ceramic support. Before performing the catalyst deposition step unsupported CeO₂-ZrO₂ powders have prepared and characterized in order to confirm the formation of the required uniform mixed-oxide with both defined composition and textural characteristics. The optimized sol formulations were subsequently used for the impregnation of the porous ceramic supports. During deposition, the sol viscosity was also controlled in order to limit the formation of a surface coating which was shown to suffer from attrition. The as-prepared catalyst has been tested for DMC synthesis in a continuous stirred tank reactor evaluating its catalytic activity as a function of the quantity and specific surface area of the active phase deposited on/in the porous ceramic support.

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Electrochemical impedance spectroscopy of solar cells employing anatase (101) and anatase (001)

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Abstract

Nanocrystalline TiO₂ belongs to widely studied semiconducting metal oxides. TiO₂ anatase is an attractive material for applications in photoelectrochemical solar cells and Li-ion batteries. The usual TiO₂ anatase crystal is dominated with (101) facet, due to its thermodynamic stability, but presently the (001) facet is the other point of interest. The material properties of the most commonly synthesized TiO₂ anatase with a (001) facet were studied by electrochemical impedance spectroscopy (EIS) and compared to a reference anatase material with (101) facet. The different energetic of both materials was revealed on the base of the EIS measurement of solar cells employing (101) or (001) anatase. The higher chemical capacitance was observed for anatase (001), which indicates a higher density of states than for anatase (101). This difference in capacitance was connected also with higher electron lifetime for anatase (001) and slower diffusion of electrons in the material.

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Catalytic hydrodenitrogenation of propylamine and propionitrile as model reaction of hydrotreating pyrolysis oil obtained from animal by-products

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Abstract

Organic wastes and by-products of food industry and agriculture are renewable sources of second generation bio-fuels. Pyrolytic biomass conversion gives biochar, gaseous and liquid products. The liquid is called bio-oil. Since the raw bio-oil is usually, viscous, corrosive, and chemically unstable liquid, its upgrading is indispensable to get hydrocarbon similar to conventional fuel. The goal of the present work was to develop the scientific background of a technology for refining pyro-oil obtained from meat- and bone-meal (MBM). The oil has high nitrogen (8-12%) and relatively low oxygen content (<4%). The catalytic hydrotreating of the oil provides hydrocarbon, ammonia and water. The hydrocarbon and the ammonia are useful fuel and fertilizer precursors, respectively.

In the present work propylamine and propionitrile were used as model compounds of pyro-oil. The HDN reaction was studied over supported (silica gel, SBA-15, laponite) nickel phosphide (Ni_2P) catalysts. Operando DRIFT spectroscopy was applied to learn about the species on the surface of the working catalyst. The reaction was shown to proceed mainly through dipropylamine intermediate. TEM pictures and infrared spectra of adsorbed CO showed that the active Ni_2P phase was restructured in contact with N-bases.

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Mechanism of NO-SCR with methane over Co,H-ZSM-5 and Co,H- mordenite catalysts

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Abstract

The use of cheap and abundantly available methane as reducing agent can be especially beneficial to control the NO_x emission of boilers and engines fuelled by natural gas. Cobalt-zeolites were among the most studied catalytic systems due to their favorable catalytic properties shown in the NO-SCR reaction with methane. Some details of the catalytic mechanism including the role of different Co species and NO₂ as reaction intermediate are still matter of debate. The aim of the present study was to give further insight into the mechanism of the reaction.

The reaction was shown to proceed in consecutive steps via bifunctional mechanism over active sites (i) promoting the oxidation of NO by O₂ to NO₂ (NO-COX reaction), and sites (ii) whereon disproportionation and charge separation of 2NO₂ generates activated surface intermediate NO₃⁻/NO⁺ ion pair. Latter process was found to require Co²⁺ zeolite cations. The NO-COX reaction was shown to proceed over Co-oxo species and cobalt oxide, if present, and also over Brønsted acid sites but at a significantly lower rate. In the reaction of methane and the NO₃⁻/NO⁺ ion pair (CH₄/NO-SCR reaction) CO₂, H₂O, and N₂ was formed and the active Co²⁺ sites were recovered. The surface concentration of the NO₃⁻/NO⁺ ion pair must have been controlled by the relative magnitude of the apparent rate constants of the consecutive NO-COX and CH₄/NO-SCR reactions. Below about 700 K reaction temperature latter reaction governed the rate of the consecutive NO reduction process. Above about 700 K combustion became the main reaction of methane. Because of the low equilibrium NO₂ concentration at these high temperatures the NO-COX reaction took over the control over the rate of the NO-SCR process.

Photocatalytic water splitting by Ln-doped TiO₂ (Ln = Pr, Dy, Sm)

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Abstract

Ln-doped TiO₂ nanoparticles (Ln = Pr, Dy, Sm) were prepared by the sol-gel low-temperature reaction of titanium tetraisopropoxide with aqueous solutions of organic acid and lanthanide salts. Reaction was carried out with 0.3%, 0.5% and 0.7% lanthanide ions in acidic solution at 100 °C for 10 hours. XRD analysis revealed the content of crystalline phase of anatase and brookite in the molar ratio of approximately 1:1. Prepared nanoparticles contained crystallites ranging in size from 2.0 to 5.0 nm. Specific surface area of Ln-doped TiO₂ ranged from 220-280 m²/g. All titania samples were calcined at 600 °C for 90 min. Differential photocatalytic activity of titania nanoparticles was evaluated at photocatalytic water splitting (of 20% aqueous solution of methanol) in batch quartz reactor. The hydrogen content in the gas phase was measured by mass spectrometry. Co-catalyst, 0.5% of Pt, was deposited on the surface of titania by photochemical method. It was found that the photocatalytic activity increased with the content of lanthanide ions in biphasic catalyst. Titania doped by Dy had approximately double photoactivity then Sm-doped TiO₂ or Pr-doped TiO₂. Ln-doped TiO₂ nanoparticles prepared at 100 °C were more active then the catalysts prepared at 600 °C.

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Baeyer-Villiger oxidation over Ca(II)Sn(IV)-layered double hydroxide prepared by the combination of dry and wet milling

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Abstract

Ca(II)Sn(IV)-layered double hydroxide [Ca(II)Sn(IV)-LDH] samples have been prepared with the combination of dry and wet milling. Dry milling was necessary for the thorough mixing of the components, while wet milling was crucial for the construction of the layered structure. The synthesised material was characterised by a range of instrumental methods (X-ray diffractometry, thermogravimetry, infrared and Raman spectroscopies, scanning electron microscopy and its combination with energy dispersive X-ray analysis). Data produced by these measurements verified unambiguously that layered double hydroxide was formed indeed.

The substance then was tested as catalyst in the Baeyer-Villiger oxidation of cyclohexanone to ϵ -caprolactam with H₂O₂. The reaction was followed by gas chromatography. The LDH displayed appreciable activity in the reaction, and could be recycled without significant reduction in the transformation rate.

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Monolithic cobalt spinel catalysts for N₂O abatement from nitric acid plants

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Abstract

Cobalt spinel oxide was found to be one of the most active catalysts for low temperature N₂O decomposition reaction. Its reactivity can be effectively promoted via bulk (Zn, Ni) and surface (alkali) modifications. However, practical application of optimized double-doped cobalt spinel catalyst is limited due to relatively high price of cobalt. This problem can be solved by dispersion of the active phase on a monolithic body. A series of monolithic catalysts with the 0.3% loading of the cobalt active phase dispersed on a cordierite substrate was prepared by impregnation method: K-Co_{2.6}Zn_{0.4}O₄/cordierite (CAT1), K-Co_{2.6}Zn_{0.4}O₄/ZnO/cordierite (CAT2) and K-Co_{2.6}Zn_{0.4}O₄/CeO₂/cordierite (CAT3). The catalysts were thoroughly characterized by means of RS, SEM, TEM, XRF, XPS, and their catalytic activity was investigated in residual gases in pilot plant in Puławy (200–4000 ppm NO_x + 0.3–1.5% H₂O + 0.6–2.5% O₂ + 500–1200 ppm N₂O, GHSV = 10,000 h⁻¹). The Raman Spectroscopy measurements confirmed spinel structure of the active phase in the all examined catalysts. SEM investigations revealed the presence of spinel patches dispersed over the cordierite channel walls in the case of CAT2 and CAT3 samples. The absence of the Co₃O₄ patches for CAT1 can be explained by spinel localization within the cordierite pores, which was verified with TEM. The catalytic tests revealed that the best monolithic catalyst (CAT3) met the requirements (conversion > 90% for $T < 400^{\circ}\text{C}$) of the nitric acid industry for low temperature N₂O abatement.

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Preparation and characterization of ZnO nanoparticles

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Abstract

Zinc oxide is an inorganic compound which can be used in different field of applications varying from paints (pigment) to chemicals (catalyst or starting material for different Zn compounds production), from pharmaceuticals (e.g. in antiseptic creams) to agriculture (Zn nutrient), from rubber (additive) to ceramics (in enamels). ZnO nanopowders exhibit antibacterial, anticorrosive, antifungal and UV filtering properties and special attention is these days given to so-called 'active' zinc oxide. The term 'active' is used for ZnO powder with very high specific surface area and high chemical reactivity.

In our study, we focused on the preparation and characterization of ZnO and accompanying phase. It was found that used precipitation agent and used reaction conditions play an important role and the reaction does not lead in all cases to the formation of ZnO and the formation of new compound which is not described in XRD pattern library was observed. This new phase was studied in detail. Characterization of prepared powder was done by X-ray diffraction, X-ray fluorescence, thermogravimetry and S_{BET} measurement.

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