

Preface

This special issue of the Polish Journal of Chemistry contains some of the most interesting studies presented at the 10th Polish–Ukrainian Symposium on Theoretical and Experimental Studies of Interfacial Phenomena and Their Technological Applications. The symposium was held on September 26–30, 2006 in the Uzlijsja Conference Centre, Peremyshliany District, Lviv Province of Ukraine. The location is revelant since Lviv (Lwów in Polish spelling), the “western” capital of Ukraine, is close to the Ukrainian and Polish hearts. Many outstanding Polish and Ukrainian intellectuals were born and lived in this city. Hence, Lviv contributed much to the fraternal alliance between the Polish and Ukrainian nations from the historical point of view.

Poland and Ukraine are two neighbouring countries in Central and Eastern Europe, historicaly and culturally linked. In these countries, extensive theoretical, experimental and applied studies are carried out in the fields of adsorption, ion exchange, heterogeneous catalysis and surface chemistry. Therefore, natural tendency exists among the scientists in both countries towards cooperation in the matter of fundamental and applied problems related to physical chemistry of surface phenomena.

In response to this tendency a series of symposia, of which the 10th is a significant event, was initiated by Professor Roman Leboda, Maria Curie-Skłodowska University in Lublin in 1995 to promote exchange of scientific information and discussion on problems in adsorption, chromatography, ion exchange, heterogeneous catalysis, *etc.* The first symposium was held in Kazimierz Dolny, the historic town in Eastern Poland. Since then, the symposia have been held annually, alternating between Poland and Ukraine. The geography of the symposia included also other locations in Ukraine (Sergijivka the sea-side town in the Odessa province, and Lviv) and in Poland (Lublin and Zamość).

During the last 12 years, the interest in the symposia has been increasing. While the first Symposium was attended by only 30 participants, the number 50–70 was characteristic of the other symposia (from the second to the ninth). The 10th Symposium attracted 85 scientists from Ukraine and Poland with research interests in fundamental and applied studies of surface phenomena.

The scope of the symposia was initially defined to cover various theoretical and experimental issues of colloid chemistry, in particular, adsorption and gas chromatography, heterogeneous catalysis and ion exchange. However, with the development of their range the Scientific Committee realized that the area of the studies presented at the symposia should be extended to include other topics, in particular, human health care and environment protection, and especially the nanosystems and nano-

technologies, which have become recently the priority for the front-side industrial advances. The results of the theoretical and experimental works presented during the sessions are successfully implemented in the industry, in particular, in the environmental protection, aerosol catalysis, water conditioning devices, in the pharmaceutical industry as well as in the chromatographic analysis. The cooperation between Poland and Ukraine in what regards the studies in physicochemistry of surface phenomena, in the framework of these annual symposia, have resulted in establishment of a number of formal and informal research teams, which publish the results of their studies regularly in leading international journals.

The symposia have become popular not only among Polish and Ukrainian scientists. Recent meetings have also been attended by the colleagues from France, Germany, Lebanon, Lithuania and Russia. The geographical spread of contributions to the symposia proceedings is even wider, with the studies published increasingly, summing up the results obtained by international teams.

Not only were the scientific issues in mind of the organisers of the symposia. One of the main aims of the Scientific Committee was to promote personal contacts between the Ukrainian and Polish researchers in a human dimension, to become closer as far as thinking, lifestyle, and other human areas are concerned.

The other main aim of the Scientific Committee was involvement of young researchers to enable their scientific maturity achievement. It is a pleasure to note active participation of Polish and Ukrainian young scientists in this international scientific event, which undoubtedly promotes their professional skills. Also, while the official languages of the Symposium are Polish, Ukrainian, English and Russian, the Scientific Committee admits with great pleasure the increase in the number of young scientists able to present their studies in English, which is the language generally accepted at international scientific meetings.

The symposia are supported by the Ukrainian and Polish government bodies responsible for education and science, by national Academies of Sciences and by Polish Chemical Society.

On this occasion, the Symposium Co-Presidents express their warmest thanks to Professor Władysław Rudziński, who was one of the initiators of the Symposia, for his continuous help in organization of the events. The publication of this special issue has become possible owing to his efforts. It will certainly promote the popularity of these symposia amongst the scientific community.

It is also worth noting that the web-site of the Symposium is maintained on the regular basis; the address is:

http://www.thomascat.info/thomascat/Scientific/Ukr_Pol/Ukr_Pol.htm

*Professors Yu.I. Tarasevich and R. Leboda
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Influence of Chemical Modification on Porous Structure and Surface Properties of Activated Carbons

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Adsorption properties and concentrations of surface oxygen groups were determined for commercial carbons (WG-12 and WG-15) and commercial carbons modified by water, hydrochloric acid and nitric acid (V). Basic parameters of the porous structure of the present carbons were determined according to low-temperature isotherms of nitrogen adsorption. Moreover, concentrations of surface oxygen groups were determined by the Boehm and TGA methods. Modifying agents used here substantially affect the porous structure and chemical properties of the surface of activated carbons. The use of nitric acid (V) affects chemical properties most.

Key words: activated carbons, chemical modification, surface oxygen groups, porous structure

Influence of Teflon Surface Roughness on the Contact Angle and the Bubble Attachment in Water

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In this study the advancing and receding contact angles of water were measured on Teflon plates. Dynamic phenomena occurring during the bubble collision, attachment and the three phase contact formation (TPC) at the Teflon plates of different surface roughness were monitored, using a high speed camera SpeedCam (1182 Hz). Variations of the receding contact angles and the diameters of bubble attachment perimeters to Teflon were found to correlate to some extent.

Key words: contact angle, bubble attachment

Preparation and Characterization of Porous Polymer Composites Filled with Chemically Modified Silicas

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Effect of the silica filler with varied concentration of surface trimethylsilyl and silicon hydride groups on porosity and solvent resistance of divinylbenzene-styrene (DVB-St) and divinylbenzene-di(methacryloyloxymethyl)naphthalene (DVB-DMN) copolymers was studied by adsorption of *p*-chloroaniline. Filling with silica was shown to increase considerably solvent resistance of DVB-St copolymer, and the filler surface chemistry was found to affect essentially its porosity. Introducing of modified silicas may both increase and decrease solvent resistance of DVB-DMN copolymer, and overall functionalization of filler surface with trimethylsilyl or trimethylsilyl (20%) and silicon hydride (80%) groups have maximum effect on porosity of this copolymer.

Key words: porous copolymer, modified silica filler, adsorption, solvent resistance

Selective Hydrogenation of Crotonaldehyde over Gallia and Germania Supported Ruthenium Catalysts in a Gas Phase

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Hydrogenation of crotonaldehyde in a gas phase at atmospheric pressure over Ru/support catalysts was studied. Ruthenium nitrosylazotane $\text{Ru}(\text{NO})(\text{NO}_3)_3$ and three supports: $\alpha\text{-Ga}_2\text{O}_3$ ($60.4 \text{ m}^2/\text{g}$), $\beta\text{-Ga}_2\text{O}_3$ ($2.2 \text{ m}^2/\text{g}$) and $\alpha\text{-GeO}_2$ ($3.8 \text{ m}^2/\text{g}$) were used for catalyst preparation with the nominal ruthenium content 5 wt. % and for the catalysts supported on $\alpha\text{-Ga}_2\text{O}_3$ also 2 and 1 wt. %. The row of the catalytic performance of catalysts is as follows: 5 wt. % Ru/ $\alpha\text{-Ga}_2\text{O}_3$ > 5 wt. % Ru/ $\beta\text{-Ga}_2\text{O}_3$ > 5 wt. % Ru/ $\alpha\text{-GeO}_2$. The best catalyst, 5 wt. % Ru/ $\alpha\text{-Ga}_2\text{O}_3$, shows high selectivity to desired product-crotyl alcohol (above 85%) with the activity *ca.* $300 \mu\text{mol s}^{-1} \text{ g}_{\text{Ru}}^{-1}$.

Key words: ruthenium, selective hydrogenation, crotonaldehyde, gallium oxide, germanium oxide, unsaturated alcohol

The Structural and Energetic Properties of Zeolitic and MCM-41 Surfaces

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The adsorption of polar trichloroethene and non-polar tetrachloroethene on natural zeolites and MCM-41 was investigated at 298 K using the static method and at 355–413 K using the dynamic method. The textural properties of adsorbents were determined by nitrogen adsorption at 77 K and the energetic properties were investigated using inverse gas chromatography (IGC). The paper aimed at comparing the results of adsorption properties of investigated adsorbents under static and dynamic conditions.

Key words: adsorption, chlorinated hydrocarbons, zeolite, MCM-41

The Activity of SO₂ Removal from Combustion Gases by the DESONOX Type Catalyst Supported on Montmorillonite and Zeolite

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In this paper the authors compared the modified montmorillonite and synthetic zeolite used as supports of the DESONOX type catalyst with the standard catalyst based on MgO. The addition of DESONOX catalyst doped with vanadium ions to combusted hard coal (mass ratio coal to catalyst was 500:1) results in SO₂ removal from exhaust gases within the range from 57% to 67% for catalysts based on modified montmorillonite. The DESONOX catalyst based on zeolite is better than those based on montmorillonite. A study of supports and catalysts texture shows that the active material with vanadium ions accumulates on the pores exit and decreased pores radius and size, as well as specific surface areas of obtained materials. Prepared catalysts are better than the standard DESONOX catalyst.

Key words: desulphurization, montmorillonite, zeolite, DESONOX method

Application of Semiconductor Pt/SnO₂-based Sensor to Investigation of CO Oxidation Reaction

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Pt/SnO₂-based pellistors and resistive sensors were applied to analysis of CO oxidation mechanism. Oscillatory behavior of the system was observed, the probable mechanism explaining the occurrence of oscillations was proposed.

Key words: CO oxidation, Pt/SnO₂, semiconductor sensor

The Electrical Double Layer at the Hydroxyapatite/NaClO₄ Solution Interface

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Physicochemical properties of hydroxyapatite [Ca₁₀(OH)₂(PO₄)₆] samples surface were studied and physicochemical quantities characterizing the electrical double layer of the hydroxyapatite/NaClO₄ solution interface were determined. The investigated samples were synthesized by two methods. Hydroxyapatite (HAP) was investigated using X-ray diffraction (XRD), X-ray fluorescence (XRF), adsorption-desorption of nitrogen (ASAP), photon correlation spectroscopy (PCS), infrared spectroscopy (IR), and AFM microscope. The surface area, the average volume of pores and the size of particles of hydroxyapatite of the samples were determined. The surface charge density and the ζ potential were studied as a function of pH and the point of zero charge and the isoelectric point of samples were determined. On the basis of potentiometric titrations the values of surface ionization and complexation constants were calculated.

Key words: hydroxyapatite, electrical double layer, surface charge density, ζ potential

The Influence of Reduction Pretreatment of Pt/SnO₂ Catalysts on the Catalytic Performance in CO Oxidation

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The influence of reduction pretreatment of Pt/SnO₂ catalysts on the catalytic performance in CO oxidation reaction was investigated. We can state that the catalytic activity of samples greatly depends on the kind of reducing agent and temperature of reduction. The obtained results were explained supposing that platinum can interact with tin dioxide and strong metal-support interactions (SMSI) are created. We concluded that hydrogen can create SMSI effect more easily than carbon monoxide.

Key words: CO oxidation, Pt/SnO₂, SMSI

Fractioning of Trace Metals in Sewage Sludge

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The influence of storage time on mobility of chosen heavy metals in sewage sludge by application of Tessier fractioning procedure has been studied. Cr, Pb and Ni were mainly associated to the residual and organic matter fraction and the low mobility for these metals during the storage period has been observed. Zn showed high environmental availability and was associated mainly with reducible, carbonate and exchangeable fractions. The regularity in changes of Cu fractioning during the storage time of sewage sludge was observed. It was stated that transformation of copper chemical forms during the sludge storage takes place and some of Cu species from the organic fraction transformed into exchangeable, carbonate and reducible fractions.

Key words: sewage sludge, heavy metals fractioning

Interaction of Pyridoxine with Hydrophilic-Hydrophobic Highly Dispersed Silica

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Interaction of pyridoxine with hydrophilic-hydrophobic highly dispersed silica surface in aqueous solution has been investigated. It has been found that absorption on partially hydrophobized silica increases reaching the maximum at 12% of surface trimethylsilylation as opposed to the unmodified silica. The increase in adsorption was attributed to stabilization of pyridoxine adsorption complexes on silica surface due to additional hydrophobic and dispersive interactions with grafted trimethylsilyl groups.

Key words: pyridoxine, hydrophilic-hydrophobic silica, adsorption

Formation of Protective Coating on Amorphous Metallic Surfaces by Controlled Adsorption of Functional Oligoperoxides from Aqueous Solutions

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Formation of nanostructured functional coatings from water solutions of carbon-chain oligoperoxide surfactants (OPS) composed of vinyl acetate (VA), 2-*tert*-butylperoxy-2-methyl-5-hexen-3-yne (VEP), maleic anhydride (MA) and oligoperoxide metal complexes of (OMC) with different contents of coordinated Cu²⁺ and Fe³⁺ cations on the Fe_{78.5}Ni_{1.0}Mo_{0.5}Si_{6.0}B_{14.0} and Fe_{73.1}Cu_{1.0}Nb_{3.0}Si_{15.5}B_{7.4} amorphous alloys (AMA) has been studied. The existence of several stages of the coating formation depending on oligoperoxide nature and the solution concentration has been established. The nature and concentration of oligoperoxides define the structure and packing density of oligomer molecules in the adsorption layers. The oligomer films coordinated by Cu²⁺ on the Fe_{78.5}Ni_{1.0}Mo_{0.5}Si_{6.0}B_{14.0} and Fe_{73.1}Cu_{1.0}Nb_{3.0}Si_{15.5}B_{7.4} AMA are more rigid.

Key words: oligomers adsorption, oligomers structurization, amorphous metallic alloys

Zeolites as the Modern Catalysts for the High Octane Gasoline Component Production

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Processes of isobutane with butenes alkylation with the purpose of obtaining the high octane gasoline component (alkylate), being environmentally detrimental due to use of concentrated H₂SO₄ or HF acids as catalysts, are nevertheless of great industrial importance supplying the world market with approximately 80 mln tons of alkylate yearly. The perspective of zeolite catalysts as the substitutes of the above concentrated acids in the modern alkylation process has been considered. The most effective today's solid alkylation catalyst of the narrow acid spectrum has been found. Such acidity spectrum is considered to be responsible for the essential prolongation of the effective catalyst lifetime.

Key words: zeolite, isobutane, butenes, alkylation

Photocatalytic Activity of TiO₂ Powders and CdS Nanoparticles in the Destruction of Dyes. Influence of Alcohol Presence

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The influence of ethanol on photocatalytic destruction of dyes (methylene blue, safranine, eosine, phenosafranine) in the presence of TiO₂ powders and CdS nanoparticles in aqueous solutions was investigated. Anatase showed higher activity in water-ethanol solutions compared to rutile. The most active nanoparticles were CdS and CdS partially substituted by indium. It was established that ethanol increases the rate of photocatalytic destruction if it does not compete with the substrate for sorption centers on the photocatalyst surface.

Key words: ethanol, photocatalysis, nanoparticle, dye, titanium dioxide

Cobalt Containing Zeolite Systems: Red-ox Properties and Catalytic Activity

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The influence of zeolite nature on catalytic activity of Co-containing systems of CO oxidation was investigated. It is established that the activity of catalysts increases in the order 10%Co-NaA < 10%Co-NaM < 10%Co-NaZSM-5(37) < 10%Co-NaZSM-5(69). The cobalt spinel CoCo_2O_4 formed on the surface of zeolite supports is established to be an active phase. The TPR- H_2 study of Co-zeolite systems showed that the content of cobalt cations with high reducibility in the surface layer was the largest for the most active catalyst Co-NaZSM-5(69).

Key words: CO oxidation, Co-containing catalyst, zeolite

The Electrochemical Oxidation of Selected Antioxidants at a Glassy Carbon Electrode in Microemulsions

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The electrochemical oxidation of three antioxidants of various hydrophilic/hydrophobic characters in microemulsions stabilized by the anionic surfactant SDS was investigated using the cyclic voltammetry method. It was found that in microemulsions the oxidation process is more difficult than in electrolyte solutions. The oxidation potential (E_{pa}) of hydrophobic antioxidants propyl gallate (PG) and α -tocopherol (α -T) at a glassy carbon electrode increases monotonically with the decrease of water content, whereas for the ascorbic acid (AA) the peak potential behaviour is more complicated. At first, E_{pa} increases with the decreasing oil content up to the bicontinuous phase composition and then decreases rapidly. The currents (I_{pa}) for hydrophobic antioxidants are low in the whole composition range of microemulsion. For hydrophilic AA, I_{pa} is much higher, especially in the oil-in-water system. In the paper the changes of redox parameters of selected antioxidants are related to the micro-heterogeneity of the colloidal system and the structure of the adsorption layer formed on the electrode surface.

Key words: antioxidants, microemulsion, electrochemical oxidation, cyclic voltammetry

Application of the Molecular Sieves as Matrices for Chromophores Embedded in Their Cages

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Zeolite matrices have been applied for embedment of sulfur radical chromophores inside the intra-crystalline cages. The thermal treatment of zeolites (200–800°C) with sulfur radical precursors (oligosulfides, elemental sulfur and alkalis) led to colored products. Their coloration (yellow, green, blue) and structure depended on structure type of parent zeolite (LTA, FAU, SOD, ERI, CAN, GIS, STI, CHA, HEU), alkalinity of the initial mixture, temperature and time of thermal treatment. Synthesis at high temperatures under high alkalinity of mixtures always resulted in recrystallization of parent zeolites towards sodalite, whereas the mild preparation conditions did not affect the original structures of zeolites. Employing of zeolites as starting materials allows to extend the palette of achievable colors of ultramarine pigments.

Key words: zeolites, pigments, sulfur radicals, ultramarine analogs

Effect of NO, O₂, SO₂ on Nitrous Oxide Conversion over Fe- and Co-containing Zeolite and Zirconia Catalysts

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The conditions of positive effect of NO, SO₂ and O₂ on conversion of nitrous oxide over iron-containing zeolite-based catalysts were found in contrast to cobalt-containing catalysts. The results have been interpreted from the standpoint of N₂O decomposition mechanism. In simultaneous reduction of nitrogen(I,II) oxides by C₃–C₄ alkanes higher conversions of NO and N₂O are achieved over Co-containing and Fe_xO_y/H-ZSM-5 catalysts, respectively.

Key words: nitrous oxide; decomposition; reduction, lower alkanes, Fe-, Co-zeolites, zirconia, NO, SO₂, O₂

Preparation of Mineral-Carbon Adsorbents from Flotation Tailings Using the Spherical Agglomeration Technique

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Flotation tailings, obtained from the copper recovery process, were converted into aggregates by means of the spherical oil agglomeration process, using sodium oleate or dodecylammonium hydrochloride as particles' surface modifiers, and kerosene as bridging oil. The agglomeration process was characterized in respect to the surfactant nature, its concentration and amount of kerosene used. Resulting agglomerates were carbonized at 700°C in the Grey-King retort to give the mineral-carbon adsorbent. Subsequent alkaline work-up resulted in substantial increase of sorptive properties, as determined by the adsorption of water vapour, benzene and methanol and BET surface measurement. Simultaneously, removal of As³⁺ ions from aqueous solution has been examined. The results obtained in the present study clearly indicate possibility of making cheap and valuable composite sorbents from flotation tailings.

Key words: mineral-carbon adsorbents, spherical oil agglomeration, flotation tailing, adsorption

Temperature Dependence of Polyacrylic Acid Adsorption on the Alumina Surface. Free Energy of Polymer Adsorption

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The temperature dependencies of the polyacrylic acid (PAA) adsorption layers structure on the alumina surface were studied. The amount of polymer adsorbed and the thickness of polymer adsorption layers were determined in the 15–45°C temperature range. The obtained increase of PAA adsorption and the increase of thickness of polymer adsorption layers with the rise of temperature are caused by conformation changes of polymer macromolecules. Such behavior of the investigated systems was confirmed by the calculated parameters characterizing conformational changes of polymer chains in the bulk solution and on the solid surface. The free energy of PAA adsorption was estimated on the basis of adsorption-desorption measurements (desorption of previously adsorbed radioactive inorganic ions by polymer macromolecules). The obtained values were compared with the respective values calculated from the ζ potential data.

Key words: polyacrylic acid, alumina, polyelectrolyte adsorption, free energy of adsorption, thickness of polymer adsorption layers

Kinetic Study of Hydrogenation of Nitrate over Pd-In/Al₂O₃ Catalysts

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Liquid-phase reduction using monometallic and bimetallic catalysts (5%Pd/Al₂O₃, 2%In/Al₂O₃, 5%Pd-0.5%In/Al₂O₃, 5%Pd-1%In/Al₂O₃, 5%Pd-2%In/Al₂O₃) was studied in a slurry reactor operating under atmospheric pressure. Kinetic measurements were performed for the low concentration of nitrate ($0.4 \cdot 10^{-3}$ – $3.2 \cdot 10^{-3}$ mol/dm³) and the temperature range 293–313 K. From the experimental data it was found that the reduction of nitrate is the first order with respect to nitrate. On the basis of the rate constants apparent activation energy was established using a graphic method.

Key words: reduction of nitrate, bimetallic palladium catalysts

Temperature Dependence of Hammett Acidity for H-Y Faujasite

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The values of Hammett function for the H-Y faujasite at different temperatures have been determined on the basis of UV-Vis diffuse reflectance spectra of the five indicators recorded at 25–230°C. It has been found that the acidity of H-Y achieves the superacid values of $H_0 < -12$ at $T \geq 170^\circ\text{C}$.

Key words: catalysis, acidity, faujasite

On the Influence of Chemical Modification of Silica on Its Porous Structure under Solvothermal Conditions

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Changes of porous structure of silica gels (aerosilogels) were studied during their chemical modification under various conditions, *i.e.* solvothermal at high temperature and pressure of reagents as well as in common treatment with substances of different chemical character without high pressure. Necessity of taking into account the effects of transfer of silica mass during its modification under the conditions of high pressure of modifying agent (organothermal treatment) on its porous structure parameters was pointed to.

Key words: silica, modification, porous structure, mass transfer

Oxidative Dehydrogenation of Propane over Mechanochemically Activated V_2O_5 - Cr_2O_3 System

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High-energy ball milling of V_2O_5 - Cr_2O_3 mixture (V/Cr molar ratio = 1/10) initially causes dispersion of vanadium oxide on the surface of chromium oxide grains resulting in an *active phase-support* system. The increase of both, the V/Cr ratio on the surface and acidity of active sites is observed. Thus, this system mechanically treated for only 30 minutes has lower selectivity of propane conversion to propylene than the non-milled one. Due to homogenization resulting from longer milling time, the vanadium layer on the surface is destroyed and therefore the lower V/Cr ratio on the surface and decrease in acidity are observed. Simultaneously, the formation of $Cr_2VO_{5.5}$ phase takes place. It was concluded that these phenomena were responsible for a significant increase of selectivity in conversion of propane to propylene in contrast to the non-activated sample.

Key words: mechanochemical treatment, ball milling, vanadium oxide, chromium oxide, oxidative dehydrogenation, propane, 2-methyl-3-butyn-2-ol

A Role of Sulphur Dioxide Adsorption on Zeolite DESONOX Catalysts as the Factor Influencing Sulphur Dioxide Removal from Exhaust Gases

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This paper reports the study of the relation between sulphur dioxide adsorption and sulphur dioxide removal degree from exhaust gases on DESONOX type catalysts based on the synthetic zeolite Sipernat impregnated with vanadium ions by the double impregnation method, with the use of the EDTA solution (first impregnation step) and NaOH with V₂O₅ solution (second impregnation step) for different periods of time: 4, 16 and 32 minutes. The studied materials are designated as: support – Sipernat, catalysts: Sipernat VX, where X is the impregnation time in minutes. The sulphur dioxide adsorption for all catalysts was smaller than that for the Sipernat support. The active material (vanadium ions) decreased the amount of sulphur dioxide adsorption centers. The samples, which adsorb smaller amount of sulphur dioxide, are better DESONOX catalysts. The sample Sipernat V16 is the best of the studied catalysts.

Key words: zeolite, adsorption, sulphur dioxide

Effect of Block Copolymer Type on Formation of Mesoporous Silica Structure

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The mesoporous silicas of well organized structure were synthesized by applying three different block copolymers of poly-(ethylene oxide)-poly-(propylene oxide)-poly-(ethylene oxide) (PEO-PPO-PEO) type as templates. The properties of Pluronic aqueous solutions were studied by applying the viscosimetric measurements. The structure characteristics of the obtained materials were analyzed using nitrogen adsorption/desorption isotherms and X-ray diffraction data. The effect of structure and properties of the Pluronic type template on the formation of porosity of mesoporous silicas is discussed.

Key words: mesoporous silicas of well organized structure, structure characteristics

Influence of Au/Fe₂O₃ and Au/TiO₂ Catalysts Preparation on Their Activity in CO Oxidation by Oxygen and Water Gas Shift Reactions

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Supported Au/Fe₂O₃ and Au/TiO₂ catalysts appear very active in both carbon monoxide oxidation by oxygen or water. The aim of this work was to find correlation between gold catalysts activity and methods of their preparation (impregnation and deposition-precipitation), the influence of alkali ions additives and temperature of calcination. The physico-chemical properties of Au/Fe₂O₃ and Au/TiO₂ catalysts were investigated by TPR, ToF-SIMS and catalytic activity methods. Carbon monoxide conversion degree in oxidation by oxygen is higher for Au/Fe₂O₃ than for Au/TiO₂ catalyst, but the activity of gold catalysts in carbon monoxide oxidation by water is opposite. The most active catalyst was Au/Fe₂O₃ prepared by deposition-precipitation method with an addition of urea and those catalysts prepared by impregnation method with an addition of KOH. The analogically prepared Au/TiO₂ catalyst exhibited comparable activity. The gold catalysts appear the most active after drying at 60°C – the role of disordered catalyst structure and hydroxyl groups. The carbon monoxide conversion degree depends on the applied precipitate agent in the following order: KOH > Na₂CO₃ > NH₃. The gold catalysts do not lose catalytic activity during long lasting tests (170 h) and do not suffer on the presence of moisture and chlorine in catalyst system. The impregnated Au(K)/Fe₂O₃ catalysts with a ratio Cl/Au = 4/1 – 8/1 show considerable activity.

Key words: gold catalysts, carbon monoxide oxidation by oxygen or water, TPR, ToF-SIMS

Ionic Liquids as New Components of the Membrane of Strontium Ion-Selective Electrodes

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The effects of the addition of ionic liquids (ILs) to the membrane phase on the potentiometric properties of strontium-selective electrodes were investigated. The studies were carried out with plasticized PVC membranes doped with bis[(trifluoromethyl)sulfonyl]amides. The electrode basic analytical parameters, such as detection limit, linear range, slope characteristics, response time and dependence of the electrode potential on pH as well as selectivity coefficients in relation to some inorganic cations were determined. As follows from the studies the addition of ILs to the membrane phase improved the analytical parameters of the studied electrodes, especially the improvement in selectivity was notable.

Key words: strontium ion selective electrodes, ionic liquids, crown ethers

Characterization of the Methacrylate Copolymers with the Use of Inverse Gas Chromatography

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Characterization of porous copolymers formed by suspension polymerization of methacrylate monomers with divinylbenzene is presented. Two representative copolymers were used as stationary phases in gas chromatography. In order to determine the influence of chemical structure of the monomers on their chemical nature the two procedures were used: the selectivity triangle and the general selectivity. As a reference phase PorapakQ – the least polar commercially available porous polymer was used. Porous structure of copolymers was also characterized using nitrogen adsorption isotherms.

Key words: suspension polymerization, porous microspheres, inverse gas chromatography, polarity, selectivity

Structure Correlated Parameters and Their Influence on the Bioactivity of Compounds

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The skin barrier function is important both to the topical delivery of drugs and to risk assessment following dermal exposure to various chemicals. It is impossible to assess the skin permeability of all new molecules synthesized in laboratory using only *in vivo* experiments. Computational modeling and QSAR methods provide an inexpensive and fast way to assess the potential for skin permeability of molecule before synthesis and enables prioritization of molecules for *in vitro* and *in vivo* tests. To illustrate the possibility of the use of calculation methods to estimate the skin permeability of compounds a congeneric series of triterpenes was chosen.

Key words: skin permeability, structure-activity, triterpenes

Biosorption of Uranium on Immobilized Microalgae

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The biological method of purification of water from uranium(VI) has been studied. The sorption capacity of the immobilized microalgae on the clay minerals as concerns uranium was established. Algal biomass of *Scenedesmus acutus*, *Chlorella vulgaris* and *Microcoleus vaginatus* and algae *Neocystis broadiensis* demonstrated high effectiveness in uranium sorption, and proved to be an excellent representative to remove uranium from contaminated water.

Key words: uranium, algal biomass, clay minerals, sorption, immobilization

Study of the Trace Palladium Enrichment Mechanism on Modified Activated Carbons with Respect to Analytical Applications

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The influence of modification of commercially available carbon on Pd(II) adsorption has been studied. Modified activation carbons are characterized by different palladium sorption capacities. The optimal pH-value for Pd(II) adsorption is 1.5 units. The influence of nitrate on Pd(II) adsorption was also studied. Linear decrease of Pd(II) adsorption with the increasing nitrate concentration was observed. The obtained Pd(II) adsorption isotherms were described by the Freundlich equation. It was stated that the parameter n characterizing heterogeneity of a carbon has the great influence on the sorption mechanism.

Key words: adsorption, activated carbon, palladium

Synthesis and Characterization of Bimetallic Ag-Mn-MCM-41 Materials

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The series of mesoporous, bimetallic Ag-Mn-MCM-41 materials were synthesized by applying direct synthesis and ion-exchange methods. Their surface and structure characteristics were analyzed using nitrogen adsorption/desorption isotherms, XRD data, FT-IR/PA spectrometry, and temperature programmed reduction. The differences between the porous structure and the forms of metallic species formed in the structure and on the silica surface were found for the materials synthesized by direct synthesis and ion-exchange method.

Key words: bimetallic mesoporous silicas, Ag-Mn-MCM-41; structure and surface characteristics

Kinetics and Equilibrium of Adsorption of Dissociating Solutes from Aqueous Solutions on Mesoporous Carbons

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Static and kinetic studies on adsorption of benzoic and 4-nitrobenzoic acids on two mesoporous carbons in acidic and neutral buffer solutions are performed. The carbon properties are analyzed by means of nitrogen adsorption. The static experiments in a wide range of concentrations are analyzed by means of the Langmuir-Freundlich and Freundlich isotherms. The Lagergren, pseudo-second-order, intraparticle-diffusion and multi-exponent equations are used in the analysis of kinetic equilibria.

Key words: mesoporous carbon, adsorption kinetics, dissociating benzene derivatives

Estimation of Features of Activated Carbon Materials Used for Drinking Water Purification

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The adsorption parameters of the activated carbon (AC) BAU and KAU-TF, which have been used for purification of tap water over a long period of time, are estimated. It is shown, that the AC with the native biofilm is subjected to spontaneous bioregeneration. As a result of this process 68–96% of surface of AC mesopores is restored. To free the porous volume of the AC completely it is necessary to wash out the AC with the solutions of alkali and acid consistently after approximately two years of AC filter work.

Key words: activated carbon, spontaneous bioregeneration, washing out

Cu-Co-Fe Oxide Catalysts Supported on Carbon Nanotubes in the Reaction of CO Oxidation

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Cu-Co-Fe oxide catalysts supported on carbon nanotubes were studied in the reaction of CO oxidation. Carbon nanotubes with diameter 20–30 nm and length of several microns were synthesized on oxides of Ni, Co and Fe. The physicochemical properties of these catalysts were determined with X-ray, TPD analysis and nitrogen adsorption-desorption. The data obtained have shown the potential of using carbon nanotubes synthesized on NiO and Co₂O₃, as a support for Cu-Co-Fe oxide catalysts in the reaction of CO oxidation. The catalytic systems based on these supports give 100% conversion of CO into CO₂ at temperatures below 100°C.

Key words: oxide catalysts, carbon nanotubes, catalytically active, conversion of CO into CO₂

Influence of Synthesis Conditions on the Structure of Mesoporous Silicas Containing Thiourea Functional Group

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The mesoporous silicas with the thiourea functional group $\equiv\text{Si}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_2\text{H}_5$ were synthesized using the template method (template is cetylpyridinium chloride, C_{16}PyCl). The aim of this research was to study the influence of a number of factors on mesoporous silicas structure: the concentration of alkoxy silanes and micelle-forming surfactant; the ratio of alkoxy silanes and the nature of medium in hydrothermal treatment of mesophases. The optimum conditions for synthesis of mesoporous silicas which had been functionalized by thiourea groups and which had a highly ordered hexagonal structure were found.

Key words: template method, mesoporous silicas, functionalized materials, thiourea functional group

Application of GC and GC-MS for the Identification of Fatty Acids in *Absidia coerulea*

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The paper presents the study on the content and composition of lipids in the saprophytic fungus of forest soil – *Absidia coerulea* 93. Both free fatty acids (FFAs) and fatty acids being a part of triacylglycerols have been characterized. High Performance Liquid Chromatography (HPLC) was employed to separate different classes of compounds from the fungus extract, whereas Gas Chromatography (GC) and Mass Spectrometry combined with Gas Chromatography (GC-MS) were used for separation and identification of the individual compounds. Length of chains of the fatty acids, both FFAs and in triacylglycerols, ranged from C₁₄ to C₂₄. In both cases two C₁₈ acids were dominant: oleic and palmitic.

Key words: fatty acids, *Absidia coerulea*, triacylglycerols

Comparison of Accumulation Ability of Toxicologically Important Metals in Caps and Stalks in Chosen Mushrooms

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Intensive research has been carried out to measure and explain the presence, distribution and incredible accumulation ability of several metals in edible mushrooms. Mushrooms in contrast to green plants can store large amounts of particular trace elements. Special attention has been drawn to assess possible danger to human health connected with mushroom consumption. The distribution of Cd, Se and Hg was investigated in edible mushrooms collected from forest sites situated in the Lodz region. The quantitative analysis of metals was carried out by the flame atomic absorption spectrometry technique with the exception of Hg, which was determined by a mercury analyzer.

Key words: edible mushrooms, Mercury Analyzer, ASA, toxic metals

Studies of Bioindicators in Determination of Environmental Degradation Degree

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Biological samples are commonly used as bioindicators to control and monitor environmental pollution as well as to identify and sometimes even predict changes connected with contamination sources. In this paper, the concentrations of Ba, Cd, Cr, Mn, Pb, Sr were analyzed using the ICP-OES and ICP-MS methods in moss, lichen and needles samples. The SEM technique was adopted for assessment of the influence of environmental pollution on morphology and presence of atmospheric particulates on the surface of investigated bioindicators. The method was tested on Mixed Polish Herbs INCT-MPH-2, Pine Needles 1575a and Lichen CRM 482 with good recoveries achieved.

Key words: bioindicators, ICP-OES, ICP-MS, SEM

On the Theoretical Development and the Applicability of the Lagergren Equation for the Kinetics of Adsorption at the Solid/Solution Interfaces

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It is shown that the Lagergren equation is obtained as the simplest form of a Taylor's expansion of the general Statistical Rate Theory expression for adsorption kinetics. The parameter of this expansion is the difference between the chemical potential of the adsorbed solute molecules and those in the free bulk phase. Retaining only the first term of this expansion and assuming a constant bulk solute concentration leads to the Lagergren equation. Then, it is shown that retaining higher terms of this Taylor's expansion leads to more essential improvement of the obtained kinetic equation, than taking into account the changing concentration of the solute in the bulk phase.

Key words: Lagergren equation, sorption kinetics, statistical rate theory

Porosity of Silica Gels from Isobars of Desorption

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Thermogravimetric studies have been carried out over a wide range of temperatures permitting determination of the pore structure of silica gels. Using the TG method the desorption isobars of various adsorptives were measured. On the basis of these data pore size distributions, PSDs for series of silica gels were calculated and compared to PSDs derived from low temperature adsorption/desorption isotherms of nitrogen.

Key words: porosity of silica gels, thermal desorption, thermogravimetry

Catalysis of 1-Octene Hydroperoxide Epoxidation Reaction by Metal Disilicides

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The catalytic epoxidation reaction of 1-octene with *tert*-butyl hydroperoxide in the presence of disilicides MoSi₂, WSi₂, VSi₂, TiSi₂, TaSi₂ and HfSi₂ was studied. The kinetics of this process in the presence of the most effective catalyst MoSi₂ was investigated. The effect of reactant and reaction product concentrations on the process catalyzed by MoSi₂ was examined. The kinetic scheme was proposed and the kinetic parameters of the process were calculated. The equation for the reaction rate as well as the equation that connects the current concentrations of hydroperoxide with the reaction time and allows to calculate the theoretical kinetic curves for *tert*-butyl hydroperoxide consumption were derived.

Key words: epoxidation, catalyst, hydroperoxide, olefin, kinetic

Artificial Soils and Fertilizers on the Basis of Clinoptilolite and Their Properties

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Clinoptilolite-based soil blends have been suggested and explored their ion exchange properties. Influence of clinoptilolite and fertilizers prepared on its basis on soil properties and wheat productivity has been investigated.

Key words: clinoptilolite, fertilizers, artificial soil

Physical and Chemical Criteria for Pesticides Determination and Risk Assessment in Ecosystem

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The possibility of using the integral physical-chemical property of pesticides, their dipole moment for creation of the system of pesticides determination in environmental objects, and also for their risk assessment in the environment is discussed. Using this approach the decision support system for pesticides systematical analyses was created. The algorithm allows to choose the universal methods of extraction, purification, quantitative and qualitative determination of pesticides in special cases. The relationship between pesticide polarity and their rate of degradation in soil was established. Non-polar pesticides are most stable in the soil, therefore they belong to the most hazardous according to the risk assessment classification, whereas polar pesticides are the least stable in soil and belong to the least dangerous.

Key words: pesticides, toxicity, thin layer chromatography

Methane Oxidative Conversion over the Composites of Y- and Sc-stabilized Zirconia Based

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The influence of the composition of composites based on Y- and Sc-stabilized zirconia doped with CeO₂ and transition metal oxides (Cu, Co, Ni) on catalytic properties in the oxidative conversion of methane (partial and deep oxidation, steam reforming) was studied. Activity of the composites correlates with the quantity and mobility of oxygen in them.

Key words: methane oxidation, prototype of anodes zirconia, yttrium, scandium oxides, transition metal oxides, mobility of oxygen

Biosynthesis of Colloidal-Silver Particles Using Microorganisms

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Two *Aspergillus niger* strains (*Asp1* and *Asp2*), isolated from the soil, were used to produce silver particles of micrometer size, using AgNO₃ as a substrate. Kinetics of formation of colloidal-silver particles was monitored using UV-Vis spectroscopy. They were characterized by means of laser diffraction and scanning electron microscopy. There is substantial difference between efficiency of both strains: *Asp1* produces particles of $d(0.5) = 5.46 \mu\text{m}$ and uniformity equal to 6.75, while for *Asp2*, $d(0.5) = 13.9 \mu\text{m}$ and uniformity equals to 1.32.

Key words: *Aspergillus niger*; colloidal-silver, kinetics, UV-Vis spectroscopy

Studies of Adsorption and Porosity Properties of Carbon-Covered Alumina Surfaces

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The carbon-covered alumina (CCA) samples were prepared *via* the carbonization of sucrose highly dispersed on the alumina surface. Using special thermogravimetry and sorptometry methods physicochemical properties of carbon-covered alumina surfaces were investigated. A numerical and analytical procedure for the evaluation of total heterogeneous properties (desorption energy distribution and pore-size distribution functions) on the basis of liquid thermodesorption from the sample surfaces under the quasi-equilibrium conditions are presented. The desorption energy distribution was derived from the mass loss Q-TG and the differential mass loss Q-DTG curves of thermodesorption of pre-adsorbed polar and apolar liquid films. For the first time, the evaluation of the fractal dimensions of carbon-covered alumina using the sorptometry, thermogravimetry and AFM data is presented.

Key words: carbon-covered alumina, thermogravimetry, sorptometry, fractal dimensions, total heterogeneity

Gas Chromatography Analysis of Reaction Mixtures from Cycloaddition Reaction of α -Ethylacrolein and Ethyl Ester α -Ethylacrylic Acid

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The gas chromatography (GC) method was applied for the analysis of reaction mixture from synthesis of 2-carboethoxy-2,5-diethyl-3,4-dihydro-2H-pyran. Relative errors of GC determinations not exceeded more than 7–8%. The reaction optimal conditions were proposed on the basis of such criteria as the conversion of α -ethylacrolein, yields and selectivities of main products by using the GC method.

Key words: gas chromatography, α -ethylacrolein, cycloaddition

The Water as a Heterogeneous Cluster Disperse System

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The laser microscope method was used to investigate μm -clusters in drinking water and aqueous solutions. It was found that total content of clusters and the content of clusters of various sizes (from 5 to 40 microns) depends on nature of aqueous system and its preliminary treatment. A relaxation period of clusters content after rapid cooling of drinking water from 100°C to 20°C was detected. The total content of clusters and the content of clusters of small sizes are stabilized in water only for 8–10 minutes after rapid cooling. This effect fades away at slow cooling of the water sample.

Key words: water, clusters, laser microscope

Impact of Humic Substances on the Secondary Pollution of an Aquatic Environment by Heavy Metals and Some Organic Compounds Caused by the Bottom Sediments

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Bottom sediments of the reservoirs are the active storage of various contaminants. They represent a potential source of the secondary pollution of an aquatic environment. Exchange processes by heavy metals and organic compounds in the sediment/water system in the presence of humic substances were investigated under model experimental conditions. The studies have been also made aimed at the content and composition of dissolved organic matter, speciation of available metals in the pore solution and in the aqueous phase contacting with silt. Both oxygen deficit and complexation with humic substances caused increase of metal, protein and carbohydrate concentrations in the water medium.

Key words: humic substances, heavy metals, sediments

The Sorption of Long-living Radionuclides ⁹⁰Sr and ¹³⁷Cs by Natural Polysaccharides

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Sorption of long-living ⁹⁰Sr and ¹³⁷Cs radionuclides by natural polysaccharides – pectines and alginates in dependence on pH and ionic strength of a solution was studied. Radionuclides sorption was shown to be a minimal at low pH values and maximal at pH = 7. Nuclides sorption decreases sharply with the increase of solvent ionic strength. The main mechanisms of radionuclide sorption by polysaccharides were determined to be ion exchange and chelation.

Key words: natural polysaccharides – pectines and alginates, sorption of ⁹⁰Sr and ¹³⁷Cs radionuclides, mechanisms of radionuclide sorption

Determination of Residual Monomers in α -Alkylacrylates Dispersions with Packing GLC

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Acrylic dispersions were obtained by emulsion copolymerization of methylacrylate (MA) in the presence of methylethacrylate (MEA), methylpropacrylate (MPA) and methylbutacrylate (MBA) in the concentration range of modifying monomers 6–30% weight. The GLC method was investigated for determination of residual monomers content in synthesized dispersions.

Key words: copolymerization, methylacrylate, gas-liquid chromatography

Study of Pd(II) Sorption from Aqueous Solutions on the Natural and Acid-Modified Transcarpathian Clinoptilolite

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The sorption of Pd(II) on the natural and acid-modified clinoptilolite under static conditions has been investigated. Optimal pH values for Pd(II) sorption are 4.5 from nitrate solutions and 10.0 from ammonia solutions for both sorbents respectively. The optimum grain size of both sorbents has been determined. It was found that the sorbent in the protonated form dried at 150–160°C and the natural sorbent dried at 100–110°C have highest sorption ability. The influence of inorganic salts of ammonium, alkali, heavy and platinum metal cations as well as some inorganic and organic anions on Pd(II) sorptive ability by the natural and H-clinoptilolite has been investigated. Pd(II) desorption from sorbents has been studied. The sorption capacity of natural and H-clinoptilolite towards Pd(II) from nitrate solutions (pH = 4.2) is 977 and 3440 µg/g respectively and for natural clinoptilolite from ammonia solutions (pH = 10.0) is 2404 µg/g.

Key words: zeolite, palladium(II), sorption, ion-exchange, clinoptilolite

Adsorption of Mn(II) on Transcarpathian Mordenite

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Adsorption properties of both non-modified and acid-modified Transcarpathian mordenite towards Mn(II) ions have been studied. The maximum value of adsorption capacity of natural mordenite towards Mn(II) under optimum conditions is 750 µg/g and for acid-modified 1500 µg/g. The most efficient desorbent of Mn(II) from the mordenite bed is solution of hydrochloric acid (1:3). This adsorbent removes 100% of adsorbed Mn(II). The methods of concentration of trace amounts of Mn(II) from aqueous solutions using the obtained results have been proposed.

Key words: adsorption, mordenite, concentration, desorption, manganese(II)

Development of the Analytic Form of Reagents on the Basis of Silica Gel Impregnated with Polyhexamethyleneguanidine Chloride

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It is shown, that polyhexamethyleneguanidine chloride (PHMGC) easy sorbs on the silica gel from aqueous solutions at the expense of multicentered binding with the surface. The sorbed PHMGC is a cationic surface-active polymer and owing to an ion exchange on the sorbate surface the anionic forms of dyes are fixed with saving of their complexing (chromophoric) centers. Simple and available method of obtaining of the solid-state analytic forms of reagents opens wide opportunities of their practical application for the sorption concentration and following determination of inorganic and organic compounds.

Key words: silica gel, polyhexamethyleneguanidine chloride, dye

Complexes of Bismuth(III) on the Surface of Silica Gels, Chemically Modified with Mercaptopropyl and N-Allyl-N-propylthiourea Groups

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General approaches to the creation of molecular sorption-spectroscopic methods of analysis are considered. One of the ways of method accomplishment, which we consider as the most significant, is the complexes formation on the surface of silica gels with covalently bonded organic compounds possessing complexing ability ($\text{SiO}_2\text{]} - \text{L}_1$). The formation of intensive yellow-coloured different-ligand complex of bismuth(III) on the SH-C surface is due to development of the sorption-photometric method of bismuth determination using the diffuse reflection spectroscopy.

Key words: silica surface, bismuth complexes, sorption spectroscopy