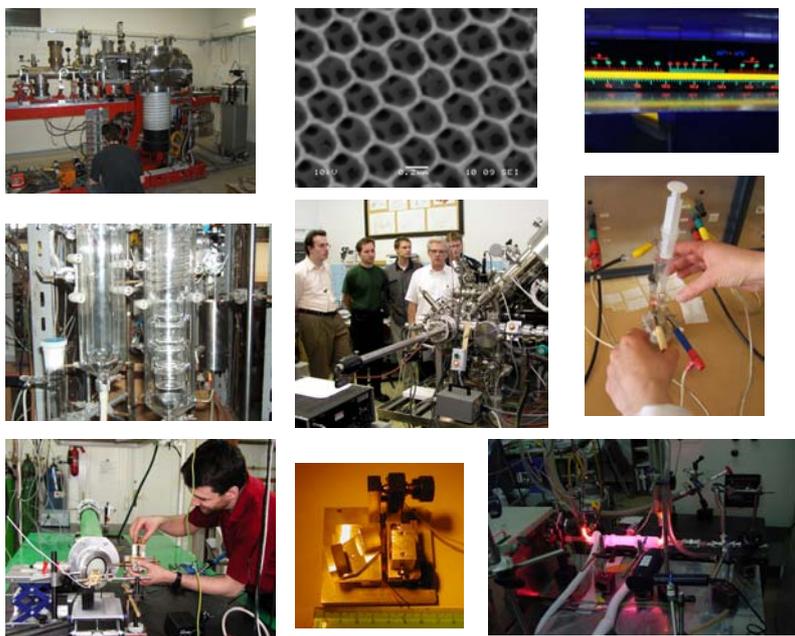


Ústav fyzikální chemie J. Heyrovského AV ČR, v.v.i.



Seminář studentů ÚFCH JH

23. -24. května 2007

Praha



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Seminář studentů ÚFCH JH

Praha, 23.-24.5.2007

Kategorie I

Studenti bakalářského a magisterského studia

Ferus Martin (*magisterské studium, školitel S. Civiš*)
Kubelík Petr (*magisterské studium, školitel S. Civiš*)
Mašát Milan (*magisterské studium, školitel O. Votava*)
Ončák Milan (*magisterské studium, školitel R. Zahradník*)
Skřínský Jan (*diplomant, školitel Z. Zelinger*)
Veis Libor (*diplomant, školitel J. Pittner*)
Vlk Josef (*bakalářské studium, školitel J. Čejka*)

Studenti 1. ročníku PGS

Bulíčková Jana (*školitel L. Pospíšil*)
Grigorová Eva (*školitel Z. Zelinger*)
Kalousek Vít (*školitel J. Rathouský*)
Macháň Radek (*školitel M. Hof*)
Olšák Jiří (*školitel Z. Samec*)
Procházková Dana (*školitel J. Čejka*)
Šiklová Helena (*školitel J. Čejka*)

Kategorie II

Studenti 2. a 3. ročníku PGS

Barucha Justyna (*školitel M. Hof*)
Brabec Jiří (*školitel J. Pittner*)
Demel Jan (*školitel J. Čejka*)
Gasiňska Barbara (*školitel M. Hof*)
Kiran Bhaskaran Nair (*školitel J. Pittner*)
Zaň Anna (*školitel M. Hof*)

Cihelka Jaroslav (*školitel S. Civiš*)
Jíša Kamil (*školitel Z. Sobalík*)
Miszta Adam (*školitel M. Hof*)
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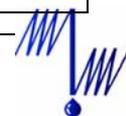


**Seminář studentů ÚFCH JH
2007**



Středa 23.5.2007

Čas	Předsedající	Přednášející	Název
8:15	Zahájení semináře studentů		
8:20	<u>Jan DEMEL</u>	Agnieszka OLZYŃSKA <i>(III.ročník, školitel M. Hof)</i>	CHARACTERIZING DRUG DELIVERY SYSTEMS USING FLUORESCENCE SOLVENT RELAXATION TECHNIQUE
8:45		Kamil JÍŠA <i>(III.ročník, školitel Z. Sobalík)</i>	SYNERGY BETWEEN Fe AND NOBLE METAL IONS IN FERRITERITE FOR DECOMPOSITION OF N ₂ O
9:10		Adam MISZTA <i>(III.ročník, školitel M. Hof)</i>	ELLIPSOMETRY, LASER SCANNING MICROSCOPY AND Z-SCAN FCS: INTERACTION OF CRYPTDIN-4 WITH SUPPORTED PHOSPHOLIPID BILAYER
9:35		Zuzana PAVLAČKOVÁ <i>(III.ročník, školitel J. Čejka)</i>	PREPARATION AND ACTIVITY OF MESOPOROUS ZSM-5 ZEOLITE IN THE ALKYLATION OF P-XYLENE WITH PROPAN-2-OL
10:00		Jiří BRABEC <i>(II.ročník, školitel J.Pittner)</i>	AUTOMATIC SYNTHESIS OF MULTIREFERENCE COUPLED CLUSTER METHODS CODE
10:25	PŘESTÁVKA NA KÁVU		
10:45	<u>Adam MISZTA</u>	Jan DEMEL <i>(II.ročník, školitel J.Čejka)</i>	BIFUNCTIONAL, HETEROGENEOUS CATALYSTS FOR HECK REACTION
11:10		Anna ZAŇ <i>(II.ročník, školitel M. Hof)</i>	STUDY OF THE MEMBRANE MODEL OF SUPPORTED LIPID BILAYERS: ARE WE ABLE TO CAPTURE THE FLIP-FLOP KINETICS BY MEANS OF FLUORESCENCE CORRELATION SPECTROSCOPY ?
11:35		Bhaskaran Nair KIRAN <i>(II.ročník, školitel J.Pittner)</i>	SINGLET-TRIPLET SEPARATION IN C ₂ USING MULTIREFERENCE BRILLOUIN-WIGNER COUPLED CLUSTER METHODS
12:00		Barbara GASIŇSKA <i>(II.ročník, školitel M. Hof)</i>	MONITORING OF DNA CONDENSATION WITH FLUORESCENCE LIFETIME CORRELATION SPECTROSCOPY (FLCS)
12:25		Jiří OLŠÁK <i>(I.ročník, školitel Z. Samec)</i>	ELECTROCHEMICAL OXIDATION OF ETHYLENE AND PROPYLENE ON Pt _{0.1} Au _{0.9} NANOSTRUCTURED ALLOY
12:45	PŘESTÁVKA NA OBĚD		
13:45	<u>Anna ZAŇ</u>	Justyna BARUCHA <i>(II.ročník, školitel M. Hof)</i>	THE INFLUENCE OF THE ANESTHETIC MOLECULES ON THE LIPID BILAYER STUDIED BY SOLVENT RELAXATION TECHNIQUE
14:10		Helena ŠIKLOVÁ <i>(I. ročník, školitel J. Čejka)</i>	THE SYNTHESIS AND MODIFICATION OF THE MESOPOROUS MOLECULAR SIEVES
14:30		Eva GRIGOROVÁ <i>(I. ročník, školitel Z. Zelinger)</i>	DETECTION OF HALOGEN RADICALS BY MILLIMETRE-WAVE SPECTROSCOPY
14:50		Vít KALOUSEK <i>(I. ročník, školitel J. Rathouský)</i>	EFFICIENT SELF-CLEANING SURFACES BASED ON ORGANIZED MESOPOROUS LAYERS OF TiO ₂
15:10	Ukončení prvního dne semináře		



Čtvrtek 24.5.2007

Čas	Předsedající	Přednášející	Název
8:15	<u>Kamil</u> <u>JÍŠA</u>	Dana PROCHÁZKOVÁ (I. ročník, školitel J. Čejka)	ACYLATION REACTION OVER ZEOLITES
8:35		Jan Skřínský (diplomant, školitel Z.Zelinger)	LASER-DIODOVÁ INFRAČERVENÁ SPEKTROSKOPIE NESTABILNÍCH ČÁSTIC
8:55		Jana BULÍČKOVÁ (I.ročník, školitel L. Pospíšil)	NITROGEN FIXATION IN THE PRESENCE OF WATER-SOLUBLE FULLERENE- γ -CYCLODEXTRIN COMPLEX
9:15		Radek MACHÁŇ (I. ročník, školitel M. Hof)	OPTICAL METHODS ELUCIDATING ACTION OF ANTIMICROBIAL PEPTIDES
9:35		Milan MAŠÁT (magisterské st., školitel O. Votava)	TVORBA RADIKÁLŮ V PLAZMATU VÝBOJE V SUPERSONICKÉ TRYSCE
10:00	PŘESTÁVKA NA KÁVU		
10:30	<u>Zuzana</u> <u>PAVLAČKOVÁ</u>	Milan ONČÁK (magisterské st., školitel R. Zahradník)	ROZEN'S OXIDATION REAGENT CH ₃ CN.HOF: THEORETICAL STUDY OF ITS REACTIONS
10:50		Josef VLK (bakalářské st., školitel J. Čejka)	FRIEDEL-CRAFTS ACYLATION OF TOLUENE OVER ION-EXCHANGED ZEOLITES AND MESOPOROUS SIEVES
11:10		Jaroslav CIHELKA (III.ročník, školitel S.Civiš)	LASER DIODE PHOTOACOUSTIC SPECTROSCOPY
11:35	PŘESTÁVKA		
11:45	<u>Jaroslav</u> <u>CIHELKA</u>	Martin FERUS (magisterské st., školitel S. Civiš)	MĚŘENÍ SLOŽENÍ SPALIN A STUDIUM NESTABILNÍCH MEZIPRODUKTŮ VÝBOJE V METHANU S HELIEM POMOCÍ SPEKTROMETRIE S FOURIEROVOU TRANSFORMACÍ
12:05		Petr KUBELÍK (magisterské st., školitel S. Civiš)	ČASOVĚ ROZLIŠENÁ FT SPEKTROSKOPIE CN RADIKÁLU
12:25		Libor VEIS (diplomant, školitel J. Pittner)	MULTIREFERENCE BRILLOUIN WIGNER COUPLED CLUSTER STUDY OF BORON NITRIDE MOLECULE
12:45	Ukončení prezentací – přestávka na OBĚD		
14:45	Vyhlášení výsledků a slavnostní ukončení Semináře studentů s připitkem a malým pohoštěním		





THE INFLUENCE OF THE ANESTHETIC MOLECULES ON THE LIPID BILAYER STUDIED BY SOLVENT RELAXATION TECHNIQUE

Mgr. Justyna Barucha

Doc. Dr. rer.nat. Martin Hof, DSc.

The molecular mechanism of action of anesthetic molecules, despite many years of research, seems to be still unclear and disputable. It was recently postulated that the effect of anesthetics on the global protein and peptide dynamics may underlie a unitary molecular mechanism of anesthesia. Since by now non anesthetic receptor has not been found it seems that the whole process, if true, might be driven by the changes in the dynamics of lipid bilayer. Solvent relaxation technique serves as an excellent tool for detection of hydration state of lipid bilayer [1] and membrane dynamics [1,2,3].

Therefore, by means of solvent relaxation technique, we decided to investigate the molecular interactions between anesthetic molecules and a model DOPC (dioleoylphosphatidylcholine) lipid membrane.

The molecular interactions between anesthetic molecules and model lipid membrane were investigated using DOPC (dioleoylphosphatidylcholine) bilayer.

The two types of the local anesthetic molecules amino amides (lidocaine and bupivacaine) and amino esters (procaine and benzocaine) were investigated. Two fluorescent dyes (Laurdan (6-dodecanoyl-2-dimethylaminonaphthalene) and DTMAC (4-[(n-dodecylthio)methyl]-7-(N,N-dimethylamino)coumarin)) with reveal different localization in the membrane were used to examine the influence of anesthetic molecules on the lipid bilayer dynamics and to determine their precise localization in the membrane.

The various effect of the local anesthetics were measured as a function of their concentration and it was compared to the general anesthetic effect of halothane.

References: [1] P.Jurkiewicz et al., *J.Fluor.* 15(6) (2005) 883; [2] P.Jurkiewicz et al., *Langmuir* 22(21) (2006) 8741, [3] J.Sykora et al., *Langmuir* 18(3) (2002) 571



AUTOMATIC SYNTHESIS OF MULTIREFERENCE COUPLED CLUSTER METHODS CODE

Mgr. Jiří Brabec

Mgr. Jiří Pittner Dr. rer. nat.

Physical properties of molecules are dependent on many factors. They make quantum chemistry (QCH) methods and their implementation complicated. The implementations of the most methods in quantum chemistry are based on numerical solving of equation systems. It means large number of operations and long computation time. Therefore the implementation must be optimized and, if possible, parallel. Because of their complexity, advanced high accurate QCH methods have to be implemented automatically, not by hand.

With an automatic code synthesis, it is possible to perform various optimizations of the calculation and test several approaches to the solution, than when writing the implementation for each case by hand. The next advantage is the error-free code synthesized in this way. Multireference coupled clusters methods belong to the most accurate quantum chemical methods. When these methods include higher term of the cluster operator, the source code can be very difficult to write by hand and optimization.

Now, the state specific multireference Brillouin-Wigner coupled cluster method (SS MR BWCC) is implementing to the NWCHEM package. In the next period I would like to extend SS MR BWCC method on state universal MR BWCC and possibly implement other multireference coupled cluster methods, and optimize the synthesized code for parallel calculations at multi-core processors. This time, project is under development.



NITROGEN FIXATION IN THE PRESENCE OF WATER-SOLUBLE FULLERENE- γ -CYCLODEXTRIN COMPLEX

Ing. Jana Bulíčková

doc. RNDr. Lubomír Pospíšil, CSc.

We report on the electrochemical conversion of dinitrogen to ammonia at ambient pressure and 60°C mediated by reduced fullerene (C_{60}) inside a molecular cavity of γ -cyclodextrin (γ -CD) in aqueous solution.

The conversion of N_2 molecule to other nitrogen compounds is termed the nitrogen fixation. Gaseous dinitrogen is highly inert molecule, whose dissociation energy $N_2 \leftrightarrow 2N$ is extremely high (946 kJ/mol). Half of the dissociation energy is used to break first bond. Reduction of dinitrogen to ammonia proceeds at ambient conditions in the nature under catalysis by the enzyme nitrogenase. The reduction of ammonia consumes six electrons and protons.

Free uncomplexed fullerene can be reduced in six consecutive one-electron redox steps yielding very reactive redox states of C_{60} . Encapsulation of C_{60} in the cavity of cyclodextrin yields a sufficient solubility of the resulting complex in aqueous medium and at the same time the redox character is kept.

The electrochemical nitrogen fixation in aqueous environment needs to overcome the energetic demands on the transfer of the first electron to the nitrogen molecule and at the same time the interfering hydrogen evolution, which decreases the concentration of available protons. Transfer of more than one electron is far less energetically demanding process and our cyclic voltammetric experiments show that the double reduced form of C_{60} of the $[C_{60}-\gamma CD_2]$ complex mediates the N_2 reduction to ammonia. This was confirmed also by the bulk electrolysis at -1.2V and 60°C.

Electrogenerated ammonia was detected by photoacoustic and high-resolution iR spectroscopy. Further studies confirmed that the reduction proceeds catalytically through the dissociation mechanism. Major part of ammonia is retained in the solution probably bound in the cyclodextrin cavity.

This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (A400400505 and KJB400400603) and the Ministry of Education (LC510 and COST OC140).



LASER DIODE PHOTOACOUSTIC SPECTROSCOPY

Mgr. Jaroslav Cihelka

Doc. RNDr. Svatopluk Civiš, CSc.

The main goal of this study is the application of laser diodes in atmospheric and analytical chemistry. Commercially available GaSb based semiconductor distributed feedback multiple quantum well lasers were used as a tunable sources of radiation with high spectral purity in temperature range of 60 °C. These types of lasers comply with the requirements for sources of radiation in high-resolution molecular spectroscopy, that means continuous wave emission, high optical power (more than 1 mW), low optical noise and high wavelength tunability (more than 20 cm^{-1}).

Lasers were used in combination with sensitive photoacoustic detection. Both devices, new type of diode lasers and new sensitive micro - microphones, were applied for high resolution gas detection in 2,3 μm spectral range.

Several photoacoustic cells were developed. Most of them were based on a simple glass resonator and two Knowles EK-3024 microphones.

These systems were tested on the rotation-vibration lines of different gases: methane, ammonia, nitrous oxide and formaldehyde. The best obtained detection limits were estimated for ammonia (0,1 ppm), formaldehyde (1 ppm) and methane (50 ppm).

Based on obtained results, the size reduced photoacoustic system was constructed. This apparatus was directly combined with diode laser (without any optical elements mirror, lens). Such small photoacoustic resonance absorption cell has similar parameters as previous system and provides better results at higher gas pressure.



BIFUNCTIONAL, HETEROGENEOUS CATALYSTS FOR HECK REACTION

Mgr. Jan Demel

Prof. Ing. Jiří Čejka, DrSc.

In last decades coupling reactions have attracted a particular attention for their wide applicability in organic synthesis. One of the most often utilized reactions is the reaction between aryl halides and activated alkenes to provide substituted alkenes. This reaction can be efficiently affected by various palladium containing catalysts, e.g., phosphine-ligated complexes, palladacycles or by fine palladium metal dispersions. The reaction typically requires the presence of base, a co-catalyst that binds the acid byproducts. In typical setup an external base such as inorganic salts or tri alkyl amines are added into the reacting mixture.

In order to prepare heterogeneous catalyst that combine both basic sites as well as palladium active centres Corma and co-workers have prepared cesium-exchanged zeolites [1] and sepiolites [2] and modified those supports with palladium chloride. Those catalysts proved to be active in Heck and Suzuki reactions but large amounts of catalyst were needed to proceed with satisfactory conversion.

In our work we have prepared heterogeneous bifunctional basic/palladium catalysts where cesium-exchanged aluminium-containing mesoporous molecular sieve MCM-41 is used as the base containing support. Subsequently onto this support we have deposited palladium nanoparticles by thermo chemical reduction of palladium acetate in THF in the presence of tetra butyl ammonium acetate as a stabilizing agent. The concentration of palladium in the catalyst was 0.1 mmol g^{-1} .

Those catalysts were tested in the model Heck reaction of bromobenzene with butyl acrylate to give butyl cinnamate. The best solvent for this reaction has proved to be *N,N*-dimethylacetamide and the reaction was done at $160 \text{ }^\circ\text{C}$. We have studied this reaction under hydrothermal conditions as well as under microwave irradiation. In both cases, the catalysts were active when 1 mol % of palladium was used, not requiring any additional external base. However, when external base (sodium acetate) was added the reaction proceeded roughly two-times faster. Microwave irradiation has significantly accelerated the reaction in comparison with hydrothermal treatment elevating conversions up to 35 % after ten hours of irradiation.

Reference:

- [1] A. Corma, H. García, A. Leyva, A. Primo, *Appl. Catal. A* 247 (2003) 41.
- [2] A. Corma, H. García, A. Leyva, A. Primo, *Appl. Catal. A* 257 (2004) 77.



MĚŘENÍ SLOŽENÍ SPALIN A STUDIUM NESTABILNÍCH MEZIPRODUKTŮ VÝBOJE V METHANU S HELIEM POMOCÍ SPEKTROMETRIE S FOURIEROVOU TRANSFORMACÍ

Martin Ferus

Doc. RNDr. Svatopluk Civiš, CSc.

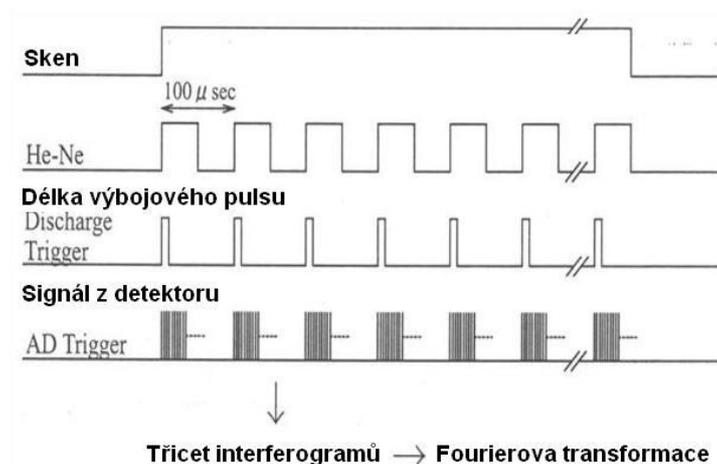
Infračervená spektrometrie s Fourierovou transformací je metodou nabízející v současnosti řadu aplikací. Pomocí této techniky bylo zkoumáno složení spalin vznětového a benzínového motoru, kouře z cigaret, marihuany a produktů hoření organických materiálů. V emisním uspořádání byl studován elektrický výboj v methanu s heliem.

K měření byl použit spektrometr Bruker IFS 120 HR umožňující emisní i absorpční měření v intervalu 500 cm^{-1} až $25\,000\text{ cm}^{-1}$ s rozlišením $0,0035\text{ cm}^{-1}$.

Obrázek znázorňuje princip měření časově rozlišených spekter. Řídící jednotka využívá digitální signál HeNe laseru pro generování sekvence výbojových pulsů. Při každém pulsu je snímáno třicet časově vzájemně posunutých signálů z detektoru. Datový výstup poskytuje třicet interferogramů, které jsou Fourierovou transformací přepočítány na třicet časově posunutých spekter.

Ve spektrech spalin byly identifikovány běžné produkty spalovacích procesů: anorganické látky jako CO, CO₂, voda a organické produkty methan, ethan, ethylen, acetylen nebo i vyšší uhlovodíky. Ve všech vzorcích kromě kouře vonné tyčinky a emisí benzínového motoru byly rovněž pozorovány absorpční pásy formaldehydu. V cigaretovém kouři byl nalezen kyanovodík, methanol a acetaldehyd.

Emisní měření výboje CH₄/He poskytlo spektra nestabilních meziproductů k jejichž vzniku dochází i během výše zmíněných spalovacích procesů. Ve spektrech byly nalezeny radikály H, C, CH, C₂ a emisní spektrum acetylenu. Význam aplikace časově rozlišené spektrometrie s Fourierovou transformací tkví zejména v možnosti sledovat souslednost reakcí v plazmatu v širokém časovém a spektrálním rozsahu během jednoho měření.



MONITORING OF DNA CONDENSATION WITH FLUORESCENCE LIFETIME CORRELATION SPECTROSCOPY (FLCS)

Mgr. Barbara Gasińska

Doc. Dr. rer.nat. Martin Hof, DSc.

DNA condensation is studied for potential implication in DNA packaging in the cell and is a prerequisite for the cellular uptake of DNA for gene therapy applications.

To obtain DNA in compact form, we can use one of condensing agents, i.e. compound with positive charge, to neutralize negative charge from phosphate groups.

One of the condensing agents is ubiquitous low molecular weight aliphatic cation, tetravalent polyamine - spermine (Spm^{4+}). Spermine neutralizes negative charge of DNA, leads to its collapse (condensation) and minimizes volume occupied by DNA molecule. At the certain spermine-to-base pair ratio, DNA coexists in condensed and non-condensed form. The aim of this contribution is to give more detailed insight into the dynamic equilibrium between the folded and unfolded DNA employing a novel technique – FLCS.

Fluorescence Lifetime Correlation Spectroscopy derives from Fluorescence Correlation Spectroscopy. In FCS contrary to the other fluorescence techniques, we analyze spontaneous intensity fluctuations detected from an illuminated volume of a femtoliter, which are then described by the autocorrelation function. Autocorrelation function provides such information on diffusion coefficients of labeled molecule in confocal volume and number of particles. FLCS combines autocorrelation with fluorescence lifetime measurements and enables to create quasi two-channel FCS, which allows for monitoring of two species of different lifetime in one sample.

We observe that Pico Green labeling the DNA molecule has different lifetimes in condensed and non-condensed form. Thus, we can extract the autocorrelation curve for both forms separately and moreover, we obtain additional information on their interaction, i.e. on the equilibrium dynamics.

DETECTION OF HALOGEN RADICALS BY MILLIMETRE – WAVE SPECTROSCOPY

Ing. Eva GRIGOROVÁ

Ing. Zdeněk Zelinger, CSc.

Spectroscopy of radicals has essential importance for obtaining information about chemistry in the atmosphere. Our interest is the detection by high resolution spectroscopy (in millimetre wave and IR regions) of species of atmospherical interest. It is planned to carry out experiment on detection of the CH_2I radical by millimetre wave spectroscopy and later to analyze the ν_4 band of the FCO_2 radical measured by FTIR spectroscopy in Wuppertal.

There are no experimental values for the rotational constants of the CH_2I radical and therefore our search for this radical is based only on high-level ab initio calculations. Radicals generally are extremely reactive and we have to choose a suitable precursor, and a suitable method of synthesis, for preparing them. We were using CH_3I as precursor and we have been trying to produce the CH_2I radical by electric glow discharge. However, in the range where we expected lines of CH_2I , the spectrum was congested due to many vibrationally excited states of CH_3I and we change our preparation process to hydrogen abstraction from CH_3I with fluorine. The search for lines is still in progress.



SYNERGY BETWEEN Fe AND NOBLE METAL IONS IN FERRIERITE FOR DECOMPOSITION OF N₂O

Ing. Kamil Jíša

Ing. Zdeněk Sobalík, CSc.

Nitric acid is one of the largest sources of N₂O from chemical industry. Tail gas from nitric acid plants contains except N₂O also NO_x, O₂ and H₂O. Fe-zeolite catalysts represent promising candidates for abatement of N₂O from nitric acid plants and also from other combustion processes. Only disadvantage of Fe-zeolite catalysts is strong deactivation under realistic conditions due to presence of H₂O. Enhancement of catalytic activity for Fe-zeolite catalysts could be achieved by doping Fe-zeolites with noble metal (Pt, Rh, Ru) thank to a synergetic effect created between Fe and noble metal.

Noble metal (Pt, Rh, Ru) zeolites were prepared by a classical ion-exchange with solutions of corresponding noble metal complexes in water. Fe-zeolite was prepared by a standard interaction with FeCl₃ solutions in acetylacetone. Bimetallic Fe/Me-zeolites were then prepared from Me-zeolite by subsequent Fe ions loading as described above. NH₄-ferrierite (TOSOH Co.) was used as a parent material for all catalysts.

Catalytic activity was studied in quartz U-shaped reactor over 100 mg of the catalysts under total flow 300 ml.min⁻¹ corresponding to GHSV 90.000 h⁻¹. Reaction mixture consisted of 1000 ppm N₂O and 0 – 500 ppm NO balanced by He. Analysis was carried out with N₂O IR analyzer Advance Optima (ABB co., Germany) and NO chemiluminescence analyzer MLU Model 200AH (TELEDYNE co., U.S.A.).

Addition of noble metal (Pt, Rh, Ru) into Fe-ferrierite enhances catalytic activity for N₂O decomposition. The highest activity was achieved over Fe/Rh-ferrierite catalyst. The activity is not equal to the simple sum of the Fe- and Rh-ferrierite at 400 °C as well as for other bimetallic catalysts that evidence synergetic effect for all studied Fe/Me-ferrierites.

In the presence of NO in the reaction mixture catalytic activity is increased for Fe-ferrite as well as for bimetallic catalysts in contrast to Rh- and Ru-ferrierites where presence of NO has negative effect. The role of NO on the decomposition of N₂O is assumed to be due to removal of oxygen atoms from active site that leads to restoration of active site and formation of NO₂.

Presence of the noble metal in the Fe-ferrierite increases conversions of N₂O and the enhancement is caused by change in the activity of NO_x species as well as the rate of recombination of oxygen atoms.



EFFICIENT SELF-CLEANING SURFACES BASED ON ORGANIZED MESOPOROUS LAYERS OF TiO₂

Ing. Vít Kalousek

Ing. Jiří Rathouský CSc.

The relatively high concentration of NO_x in the range of several hundreds of ppb in the atmosphere of present-day cities and the soiling of the external surfaces of building structures are among the major environmental issues. One of the solutions is the development of self-cleaning surfaces on the basis of mesoporous films of TiO₂, which are able to effectively degrade NO_x and grease owing to the photocatalytic oxidation. This process offers distinctive advantages when compared to other technologies, especially the ability to oxidize low-concentration and low-flow rate waste streams at ambient temperature, pressure, humidity, etc., the exploitation of weak UV irradiation of less than 1 mW/cm² sufficiently provided by the solar light (up to 4 mW/cm²). More over, no extra reactants such as NH₃ or O₃ are required.

We prepared organized mesoporous films of TiO₂ with controlled morphological properties (the character of the porosity, the pore volume, internal surface area, film thickness) by a sol-gel method exploiting block copolymers as the structure directing agents combined with the dip-coating technique. The organic component was subsequently removed by calcinations. The obtained films were characterized by electron microscopy, UV/Vis spectroscopy and physical adsorption. Their photocatalytic efficiency was tested by the photooxidation of NO in air at concentration less than 1 ppm and by the degradation of oleic acid on the deposited by dip-coating on the film surface. The effect of the UV irradiation on the surface properties of the films was determined by measuring the contact angles for both water and oleic acid.

The layer-by-layer deposition technique enabled to obtain films 1-2 μm in thickness, whose specific surface area and pore width achieved 350 cm²/cm² and 7 nm, respectively. The photoactivity of mesoporous films of TiO₂ in the NO photooxidation was found substantially superior to that of Pilkington Activ Glass, which is considered the standard material. Several hours of the 1 mW/cm² UV illumination were found sufficient to achieve the practically complete decomposition, which is faster than when standard sol-gel TiO₂ films were used.

To sum up, the mesoporous films of TiO₂ are highly promising photocatalysts for the environmental cleanup.



SINGLET-TRIPLET SEPARATION IN C_2 USING MULTIREFERENCE BRILLOUIN- WIGNER COUPLED CLUSTER METHODS

Mgr. Bhaskaran Nair Kiran

Mgr. Jiří Pittner, Dr. rer. nat.

C_2 is a simple yet an exceptional system for advanced correlated methods. This is mainly due to the strong multi-reference character of the low lying singlet state. The aim of the present work is to determine the singlet-triplet separation. The single reference coupled cluster method fails to predict the realistic singlet-triplet gap, the CCSD method even gives the wrong ordering of singlet and triplet states. MR CI methods are capable of giving very accurate results but at a significantly higher cost than MR BWCC methods.

For our calculations we used the MOLPRO program for obtaining both HF and CASSCF wave functions that were then normalized and used as input for MR BWCC methods implemented in the ACES 2 program package. Our calculations were performed using the correlation consistent basis sets (cc-pVnZ, $n = 2, 3, 4$ and 5). The equilibrium bond lengths and harmonic frequencies were also studied.



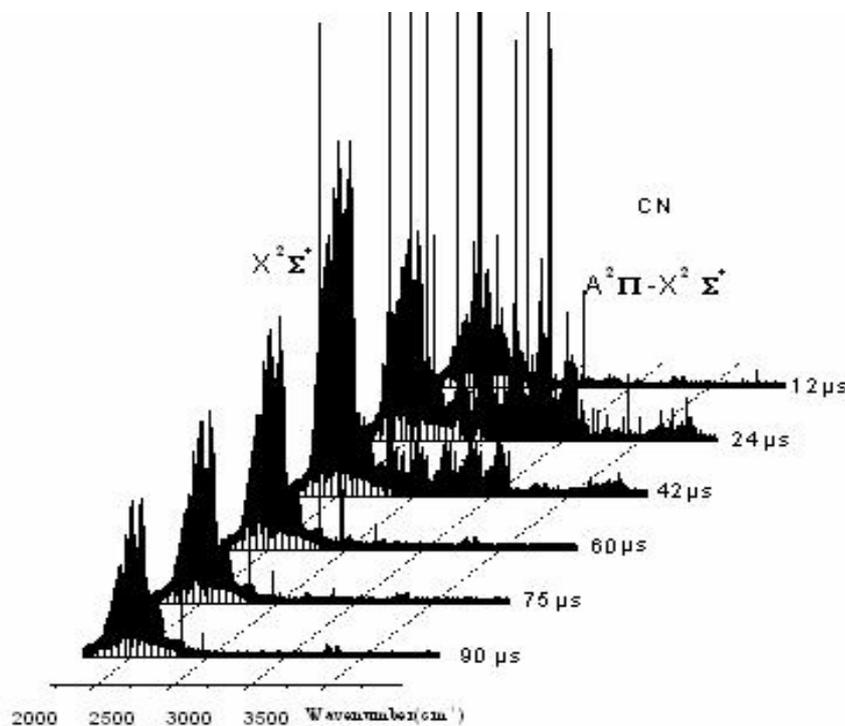
ČASOVĚ ROZLIŠENÁ FT SPEKTROSKOPIE CN RADIKÁLU

Petr Kubelík

Doc. RNDr. Svatopluk Civiš, CSc.

Časově rozlišená emisní spektroskopie s Fourierovou transformací byla použita pro kinetické studie pulzního výboje směsi He/(CN)₂ v oblasti 1800-4000 cm⁻¹. Byla změřena rotačně-vibrační spektra CN radikálu v základním elektronickém stavu (X²Σ⁺) společně s vibronickými spektry 0-3, 1-4, 2-5, 3-6, 4-7, 5-8 (A²Π - X²Σ⁺). Celkem bylo analyzováno 934 linií. Cílem této práce bylo přiřadit linie CN radikálu především v oblasti 1950-2100 cm⁻¹, kde bylo pomocí ab-initio výpočtů předpovězeno rotačně-vibrační spektrum CN⁻ aniontu.

Časově rozlišená spektra byla použita také při studiu dynamiky procesů probíhajících ve výbojovém plazmatu směsi He a (CN)₂. V plazmě byly dále identifikovány emisní linie příslušející He, C, N, C₂ a He₂.



Obrázek zachycuje časově rozlišené spektrum CN radikálu (rotačně vibrační pásy v základním X²Σ⁺ stavu a vibronické pásy příslušející přechodům A²Π - X²Σ⁺).



OPTICAL METHODS ELUCIDATING ACTION OF ANTIMICROBIAL PEPTIDES

Mgr. Radek Macháň

Doc. Dr. rer.nat. Martin Hof, DSc.

Antimicrobial peptides (AMPs) form a very large, varied and evolutionary old group of peptides, which play an important role in immunity systems of all multicellular organisms. They have attracted a lot of attention thanks to their potential therapeutical applications as efficient antibiotics, against which microbes are unlikely to develop resistance, or as anticancer agents. It has been firmly established that interaction of antimicrobial peptides with cellular membrane plays a crucial role in their biological activity, but the actual manner of this interaction is not yet fully understood. Supported phospholipid bilayers (SPBs) are often used as a model of biological membranes with well defined geometry allowing characterization by different experimental techniques.

Several experimental techniques used in our laboratory can offer information on the changes of SPBs induced by AMPs. I will say more about three of them: laser scanning microscopy (LSM), ellipsometry and Z-scan fluorescence correlation spectroscopy (FCS).

LSM shows changes in spatial distribution of lipids in the sample. Inhomogeneities in lipid distribution can be observed and the decrease in overall fluorescence intensity can indicate loss of lipids from the bilayer. Fast galvanoscanning can be used to monitor rapid changes, while slower piezo-scanning can be used to obtain better resolution and signal to noise ratio. Ellipsometry is a label-free technique measuring the mass and thickness of a dielectric layer consisting of lipids and peptide adsorbed to a solid surface. Z-scan fluorescence correlation spectroscopy is the only artifact-free single focus measurement of lateral diffusion coefficient of lipids within the bilayer. It shows how the rigidity of the bilayer was affected by peptide.

All above mentioned optical methods can be used to study samples in aqueous environment and in-situ monitor effects of treatment with peptide. Respective methods offer complementary information and their combination can provide us with a more comprehensive insight into the manner, in which different antimicrobial peptides affect biological membranes.



TVORBA RADIKÁLŮ V PLAZMATU VÝBOJE V SUPERSONICKÉ TRYSCE

Milan Mašát

Mgr. Ondřej Votava, PhD.

Volné radikály hrají klíčovou úlohu v chemických reakcích jak v zemské tak i v planetárních atmosférách. Studium jejich struktury a chemických vlastností je tedy důležité pro pochopení atmosferických dějů. Jejich vysoká reaktivita ale přináší potřebu specifických metod zkoumání, mezi hlavní omezení patří krátká doba života a tedy nutnost jejich zkoumání ihned po jejich tvorbě. Při použití běžných laboratorních metod tvorby radikálů tyto vznikají s teplotami výrazně vyššími než v podmínkách atmosféry, kterým se chceme v laboratoři přiblížit.

V rámci této práce jsem se podílel na vývoji zdroje chladných radikálů a zařízení pro zkoumání jejich charakteristik. Kombinuji zde plazmatický zdroj, který poskytuje dostatečné koncentrace volných radikálů se supersonickou expanzí, ve které jsou translační i vnitřní stavy radikálů ochlazeny na teploty hluboce pod pokojovou teplotou. K jejich charakterizaci jsem využil metody spektroskopie s vysokým rozlišením za použití diodových laserů pracujících v blízké infračervené oblasti. V rámci této práce proběhl i vývoj a výroba elektronických zařízení a softwaru pro ovládání trysky, laserového zdroje, detekci laserového záření a pro sběr dat. Změřil jsem elektrické charakteristiky výboje trysky, charakteristiky modelových radikálů i stabilních molekul v expanzi.



ELLIPSOMETRY, LASER SCANNING MICROSCOPY AND Z-SCAN FCS: INTERACTION OF CRYPTDIN-4 WITH SUPPORTED PHOSPHOLIPID BILAYER

Mgr. Adam Miszta

Doc. Dr.rer.nat. Martin Hof, DSc.

Antimicrobial peptides (AMPs) have received a lot of attention for their promising therapeutical applications. It has been shown that their interaction with cellular membranes plays an important role in the biological activity of AMPs. In our present study we used supported phospholipid bilayers as a well defined model of biological membranes and cryptdin-4 an example of AMP with beta-sheet structure.

Combination of different complementary experimental techniques provided us with quite complex information on the manner of interaction of this peptide with membrane. Ellipsometry gave us information about mass and thickness of adsorbed layer consisting of both lipids and peptides. Laser scanning microscopy showed appearance of inhomogeneities in spatial distribution of lipids in the sample and the decrease of overall fluorescence intensity indicated loss of lipids from the bilayer. Finally Z-scan FCS provided us with information on changes in mobility of lipids in membranes.

From the results we obtained we concluded that cryptdin-4 leaves membranes confluent. It makes them more rigid (decrease in diffusion coefficient) and induces inhomogeneities in lateral distribution of lipids.



ELECTROCHEMICAL OXIDATION OF ETHYLENE AND PROPYLENE ON Pt_{0.1}Au_{0.9} NANOSTRUCTURED ALLOY

Mgr. Jiří Olšák

Prof. RNDr. Zdeněk Samec, DrSc.

Electrochemical oxidation of alkenes was studied with respect to the possible oxygen insertion reaction. The feasibility of both direct and indirect electrochemical epoxidation was investigated mainly on polycrystalline metals (Pt,Au) and alloys (stainless steel). This paper extends the previous studies with the aim to address the course of ethylene and propylene oxidation on nanostructured Pt/Au alloy.

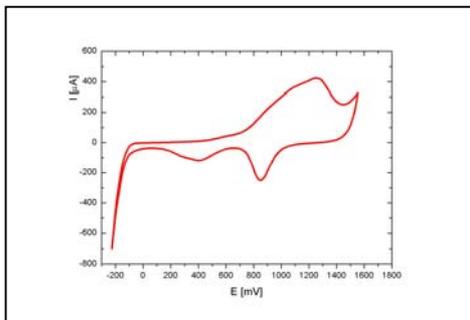


Fig 1. CV recorded on Pt/Au electrode in 0.1M H₂SO₄ solution saturated with propene, 15 mV/sec, Potential is referred vs. SCE

It is expected that nanocrystalline alloys may show unusual electrochemical behaviour due to the nonequilibrium distribution of metals in the alloy and the nanocrystalline character of the electrode material.

Solid state characteristics and electrochemical behaviour of Pt_{0.1}Au_{0.9} alloy were investigated by means of X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Cyclic Voltammetry in combination with Differential Electrochemical Mass Spectrometry (DEMS).

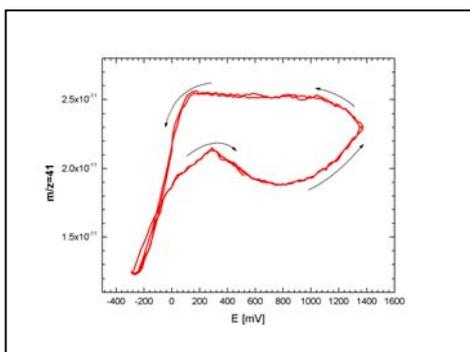


Fig 2. Potential dependence of the DEMS signal corresponding to propene abundance in the system. Experimental details were same as in Fig 1.

The voltametric data indicate that both ethylene and propylene are oxidized predominantly in the potential range where the oxidation on pure gold occurs. In contrast to the voltammetric behaviour the DEMS based analysis of the reaction products indicates preferential formation of carbon dioxide, which is the main product of alkenes oxidation on Pt electrodes. This finding points toward a "bi-functional" character of the nanostructured Pt/Au alloy where the actual active site for alkene oxidation is Pt enriched surface.



CHARACTERIZING DRUG DELIVERY SYSTEMS USING FLUORESCENCE SOLVENT RELAXATION TECHNIQUE

Mgr. **Agnieszka Olżyńska**

doc. Dr. *Martin Hof*, DSc.

Fluorescence solvent relaxation (SR) technique, based on reconstruction of time-resolved emission spectra (TRES), enables to study hydration and dynamics of the lipid membranes [1]. Solvent relaxation process refers to dynamic reorganization of solvent as a response to a rapid change in the fluorophore electric charge distribution upon electronic excitation. The overall Stokes shift gives the information on the polarity of the vicinity of the probe and thus reporting the degree of hydration of the bilayer. Moreover, the kinetics of the Stokes shift reflects mobility of the probe environment. Applied to the headgroup region of fully hydrated lipid bilayers, the solvent relaxation technique provides quantitative information on hydration and mobility of the membrane on a molecular level [1-3].

Transferosomes® are the highly deformable lipid vesicles designed for transdermal drug delivery. We use SR technique to examine surface properties of Transferosomes®, which are important for the efficiency of the drug loading. More precisely, we have recently investigated headgroup hydration and mobility of two types of mixed lipid vesicles, containing nonionic surfactants; straight chain Brij 98 and polysorbate Tween 80, with the same number of oxyethylene units as Brij but attached via a sorbitan ring to oleic acid. Additionally, we have studied interactions of those systems with protein Interferon alfa-2b (a candidate for a non-invasive drug delivery) [4].

We also apply SR technique to characterize positively charged lipid membranes. Despite the fact that structure and properties of the so-called lipoplexes (nucleic acids and lipid complexes) are extensively investigated nowadays, biophysical description of such structures is still lacking. We compare binary lipid mixtures consist of a cationic lipid (1,2-Dioleoyl-3-Trimethylammonium-Propane, DOTAP [3] or 1,2-Dimyristoyl-3-Dimethylammonium-Propane, DMTAP) and a neutral helper lipid (dioleoylphosphatidylcholine, DOPC; dimyristoylphosphatidylcholine, DMPC; or dioleoylphosphatidylethanolamine, DOPE). Because SR technique is a very sensitive method, we are indeed able to see the difference between those systems. The obtained results are in good agreement with molecular dynamics studies.

[1] P. Jurkiewicz et al., *J. Fluorescence* 15 (2005) 883.

[2] A. Olzynska et al., *Chem. Phys. Lipids* (2007) in press.

[3] P. Jurkiewicz et al., *Langmuir* 22 (2006) 8741.

[4] K. Rieber et al., *Biochim. Biophys. Acta* (2006) 1768 (2007) 1050.



ROZEN'S OXIDATION REAGENT $\text{CH}_3\text{CN}\cdot\text{HOF}$: THEORETICAL STUDY OF ITS REACTIONS

Milan Ončák

Prof. Ing. Rudolf Zahradník, DrSc.

In 1986, prof. Schlomo Rozen was looking for some media that would dissolve F_2 better than CFCl_3 . Although he had no luck with dried acetonitrile, the wet acetonitrile produced solution that was stable for few hours at room temperature. The solution was a source of electrophilic oxygen atom and it was soon discovered that the oxygen came from hypofluorous acid that was formed by reaction of F_2 with water and stabilized by association with acetonitrile. The newly discovered solution turned out to be a versatile oxidizing agent that was able to carry out even the most problematic oxidations, e.g. convert substituted thiophenes and tertiary amines to respective S- and N-oxides. Moreover, most of reactions require very short reaction times and proceed with high yields already under mild conditions.

In this work, possible general mechanisms of "Rozen's oxidation" are discussed and reaction pathways for few model reactions are determined by means of *ab initio* calculations (with HF, DFT and MP2 methods). Energy scans along reaction coordinates are performed and transition states are localized. It is demonstrated that it is highly probable that another HOF or HF molecule serves as a catalyst while hypofluorous acid dissociates to HF and oxygen atom. Model reactions are calculated both in gas phase and solution, influence of solvent (i.e. acetonitrile) is estimated using continuum solvation model. Analogous reactions with HOCl instead of HOF are also discussed.



PREPARATION AND ACTIVITY OF MESOPOROUS ZSM-5 ZEOLITE IN THE ALKYLATION OF P-XYLENE WITH PROPAN-2-OL

Ing. Zuzana Pavlačková

Prof. Ing. Jiří Čejka, DrSc.

Dimethyl (1-methylethyl) benzenes (denoted as dimethylcumenes (DMCs)), which are important intermediates in production of xylenols [1], can be obtained by the reaction of xylenes with propan-2-ol. This reaction can be catalyzed by various solid acids such as AlCl_3 [2], or zeolites USY, Y, beta and mordenite [3]. This contribution reports on the studies of the effect of reaction temperature, feed rate (WHSV), substrate to alkylating agent molar ratio (X/P) on the conversion of p-xylene and selectivity towards DMC over mesoporous ZSM-5 prepared by secondary templating method.

Mesoporous ZSM-5 was synthesized using Carbon Black Pearls (CABOT Corp.) as a secondary template and has well-defined mesoporous structure with mesopore diameter of 12 nm (mesopore volume $0.05\text{-}0.16 \text{ cm}^3\cdot\text{g}^{-1}$). The isopropylation of p-xylene with propan-2-ol was carried out in a glass down-flow microreactor under atmospheric pressure in the temperature range $175\text{-}250 \text{ }^\circ\text{C}$ with WHSV (p-xylene) $2\text{-}10 \text{ h}^{-1}$ and X/P molar ratio $0.33\text{-}2$. The reaction products were analyzed using an *on-line* gas chromatograph (HP 5890A) equipped with FID detector and Supelcowax 10 capillary column (30 m). The first analysis was performed after 15 min of time-on-stream (T-O-S) and the others followed with the interval of 40 min.

The comparison of the results of alkylation of p-xylene with propan-2-ol over conventional ZSM-5 and mesoporous ZSM-5 shows that p-xylene conversion increases with increasing temperature. The highest selectivity towards 2,5-DMC was achieved at the temperature of $200 \text{ }^\circ\text{C}$ – 50 % or 80 % over microporous ZSM-5, mesoporous ZSM-5 resp. With increasing WHSV, conversion of p-xylene decreases. The effect of X/P molar ratio demonstrated that the conversion of p-xylene increases with increasing X/P ratio and the highest selectivity towards 2,5-DMC was achieved at the X/P ratio 1.67.

- [1] K. Ito, *Hydrocarbon Processing*, 50, 89 (1973)
- [2] E.V. Kirkland, O.P. Funderburk, F.T. Wadsworth, *J. Org. Chem*, 9, 12 (1958)
- [3] Ch.R. Patra, R. Kumar, *J. Catal.* 212, 216 (2002)

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ACYLATION REACTION OVER ZEOLITES

Ing. Dana Procházková

*Ing. Martina Bejblová, PhD. and
prof. Ing. Jiří Čejka, DrSc.*

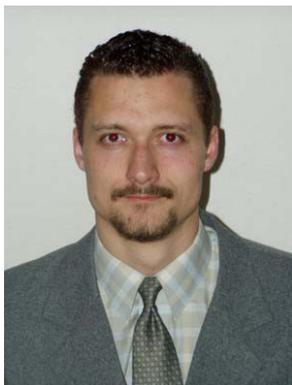
Friedel–Crafts acylation reaction was discovered at the end of 19th century. It belongs to the group of electrophilic substitution reaction. This reaction is a fundamental pillar of synthetic organic chemistry. Aromatic ketones are produced via reaction of an aromatic substrate with acylating component in the presence of a proper catalyst. Products of acylation reactions are important intermediates in pharmaceutical, fragrance, flavour, dye and agrochemical industries.

Halides, anhydrides, esters of carboxylic acids and carboxylic acids themselves are used as acylating agents. Conventionally, acylation is catalyzed by Lewis acids or strong protic acid. The major drawback of Friedel–Crafts catalysts is that they are not regenerable and must be used in more than stoichiometric amount. Heterogeneous catalysis seems to be an interesting alternative technique to homogeneous catalysis. Zeolite based catalysts offer important advantages, which include their relatively easy synthesis, shape selectivity and sometimes regio- and stereoselectivity. Deactivated zeolites can be easily regenerated.

In this contribution we studied the effect of the structure of zeolite catalysts and their acidity on activity and selectivity in cyclohexene acylation. In addition, influence of the type of acylating agent was studied.

Acylation of cyclohexene was carried out in liquid phase in multi-experiment Work Station StarFish. Anhydrides of carboxylic acid with different chain length were used as acylating agents. Zeolites Beta, USY with different Si/Al ratio and mordenite were applied as catalysts. Acylation of cyclohexene was carried out at temperature 80 °C and atmospheric pressure. Reaction products were analyzed by gas chromatography and confirmed by gas chromatography-mass spectrometry.

It was found that the conversion of acylating agent depends on the type of acylating agent. The higher conversions were obtained for acetic anhydride over zeolites Beta and while in the case of isobutyroanhydride over USY zeolites. Mordenite did not show almost any activity in the acylation with isobutyroanhydride. Acylation of cyclohexene is complicated by the formation of sideproducts like cyclohexyl acetate, diacylcyclohexene, acylcyclohexyl acetate. Selectivities to 1-acylcyclohexene were between 10 – 40 % for acetic anhydride as well as isobutyroanhydride.



LASER-DIODOVÁ INFRAČERVENÁ SPEKTROSKOPIE NESTABILNÍCH ČÁSTIC

Jan Skřínský

Ing. Zdeněk Zelinger, CSc.

Byla sestavena a testována experimentální aparatura pro infračervenou laser-diodovou spektroskopii. Metodou infračervené spektroskopie byl identifikován ion ArD^+ .

Na základě matematického a statistického vyhodnocení poměru signálu k šumu u přímo měřených absorpčních spekter iontu ArD^+ a u záznamů absorpčních spekter iontu ArD^+ s využitím fázově citlivého zesilovače byla nalezena optimální hodnota frekvenční (source) modulace a amplitudové (on-off) modulace. V práci je též hodnocena citlivost dané metody pro detekci nestabilních částic a diskutována optimalizace experimentálního uspořádání v závislosti na velikosti optické dráhy.

Dosažené výsledky mohou být podkladem pro demonstraci možností a omezení jednotlivých dílčích kroků navrhovaného metodického přístupu využití laser-diodové spektroskopie jako základního nástroje pro detekci nestabilních částic hrajících roli ve fyzikálně-chemických procesech souvisejících s hořením.



THE SYNTHESIS AND MODIFICATION OF THE MESOPOROUS MOLECULAR SIEVES

Ing. Helena Šiklová

Prof. Ing. Jiří Čejka, DrSc.

Synthesis of MCM-41 silicas was performed using surfactant blends of 1-alkyl-3-methylimidazolium and alkyltrimethylammonium salts or blends of two different 1-alkyl-3-methylimidazolium salts as structure-directing agents. Post – synthesis modification of SBA-15 proceeded with aluminum chlorhydrol in order to prepare a new material with high adsorption capacity for CO₂.

A series of templated mesoporous silicas MCM-41 was based on the precipitation of solid product from homogeneous solution of sodium metasilicate and suitable cationic surfactants. This method offers new possibilities in the control of structure and morphology of mesoporous materials. In the typical synthesis, pure surfactant or surfactant mixture and Na₂SiO₃ were dissolved in distilled water to form a clear solution. For decrease of pH, which induces the formation of solid particles, ethyl acetate was quickly added under short stirring. Then the reaction mixture was allowed to stand at 35 °C for 5 h and then at 95 °C for 48 h. Solid product was recovered by filtration, washed out with distilled water and ethanol and dried at ambient temperature. The templates were removed by calcination in air at 540 °C for 8 h. The molecular sieves were characterized by XRD, SEM, TEM and nitrogen adsorption. The characterization showed that they differ in the integral breadth of the pore size distribution curve and the presence of secondary mesopores. The silicas prepared with optimized blends of 1-methyl-3-hexadecylimidazolium chloride and octyltrimethylammonium bromide or 1-methyl-3-octylimidazolium chloride and 1-methyl-3-octylimidazolium chloride featured the perfectly ordered hexagonal porous structure with a narrow pore size distribution and a small volume of secondary mesoporous.

Modification of SBA-15 with aluminum was carried out via post-synthesis treatment with aluminum chlorhydrol. 5 g of pure silica SBA-15 was added to 125 ml of water solution of aluminum chlorhydrol [(Al₂Cl(OH)₅] and stirred at 80 °C for 2 h. The solid was recovered by filtration and thoroughly washed with distilled water, dried at ambient temperature and calcined in air at 550 °C for 4 h. Characterization of the samples was carried out by X-ray fluorescence spectroscopy (XRF), ²⁷Al MAS NMR and pyridine adsorption followed by FTIR spectroscopy. Nitrogen and carbon dioxide adsorption of the parent and modified samples with different Si/Al molar ratios were measured. Nitrogen adsorption isotherms demonstrate that the surface area of modified SBA-15 decreases with increasing amount of inserted aluminum. On the other hand, the size and shape of hysteresis loop remain practically unchanged; hence, the size and volume of mesopores are preserved. The observed decrease in the surface area is obviously caused by smoothing of the inner surface of mesopores. The amount of adsorbed carbon dioxide at 0 °C increased with increasing aluminum content in SBA-15.



MULTIREFERENCE BRILLOUIN WIGNER COUPLED CLUSTER STUDY OF BORON NITRIDE MOLECULE

Libor Veis

Mgr. Jiří Pittner, Dr. rer. nat.

Boron nitride (BN) is a substance important in materials science. The diamond-like allotrope of BN (c-BN, cubic boron nitride) is the second hardest material next to diamond and the graphite-like allotrope of BN (h-BN, hexagonal boron nitride) is a very good lubricant. Because of these facts a theoretical and experimental attention has been drawn to study this material.

BN diatomic has only 12 electrons (isoelectronic with C_2) and it seems that this molecule should be easy to calculate but the opposite is true. This system is rather complicated and BN belongs to the most difficult problems in small-molecule computational chemistry. The difficulties are caused by the fact that the lowest-lying singlet state exhibits a strong multireference character. The single-reference coupled cluster method CCSD(T) fails to predict correctly the ground state, which is surprisingly 3P . Even for the CCSDT method, the singlet-triplet separation is quantitatively unsatisfactory (too large). This system is therefore suitable for testing the accuracy of new multireference methods.

The singlet-triplet separation in BN is calculated with Multireference Brillouin Wigner Coupled Cluster methods: MRBWCCSD and recently implemented (to ACESII package of quantum chemical programs) MRBWCCSD(T) and MRBWCCSDT. Also the vibrational frequencies and anharmonicities are calculated for the lowest-lying singlet and triplet states. The correlation consistent basis sets (cc-pVnZ, $n = 2, 3, 4$ and 5) are used.



FRIEDEL-CRAFTS ACYLATION OF TOLUENE OVER ION-EXCHANGED ZEOLITES AND MESOPOROUS SIEVES

Josef Vlk

prof. Ing. Jiří Čejka, DrSc.

Catalysts possessing different concentrations of Brønsted and Lewis acid sites and structure were used in acylation of toluene with isobutyryl chloride (IBCl) or isobutyric anhydride (IBAn) with the aim of obtaining the highest selectivity to para-isopropyltolyl ketone (p-IPTK). Acylation proceeds via acylium cation. The acylium cation is formed by the protonation of an acyl species interacting with the proton of the zeolite, as the active site, and then the acylium species attaches to the aromatic ring. Metals (Zn, Al, Fe, La) were deposited on catalysts by a classical liquid-state ion exchange.

Mesoporous sieves (Al)MCM-41 and (Al)SBA-15 were obtained by hydrothermal synthesis and characterized by XRD and FTIR. Ion-exchanged commercial zeolites Beta and USY were characterized by FTIR. The reaction mixtures were analysed by GC.

The highest conversion of IBCl to p-IPTK were obtained over Al-form of zeolite Beta. In general, the relationship between loaded cation and yield of product is decreasing as follows: Al > Zn > La > Fe > H. The selectivity to p-IPTK is directing by pore size diameter and arrangement channels inside the catalyst. The role of cation on selectivity was not found.



STUDY OF THE MEMBRANE MODEL OF SUPPORTED LIPID BILAYERS: ARE WE ABLE TO CAPTURE THE FLIP- FLOP KINETICS BY MEANS OF FLUORESCENCE CORRELATION SPECTROSCOPY ?

Mgr. Anna ZAŃ

Doc. Dr. rer.nat. Martin Hof, DSc.

The cellular membrane is a very complex and dynamical structure. In order to study the particular physiochemical parameters of lipid bilayers, simplified membrane models are widely used. Supported lipid bilayers (SLB) are among the lipid self-assembly systems to study the interactions and dynamics within the bilayer. The translational diffusion, lipid rotation, the transbilayer lipid migration (flip-flop) are a few examples of membrane dynamics. The so-called flip-flop is a movement between two bilayer leaflets. It is of huge importance for the mechanism of transport across cell membranes.

By the use of optically active Indium Tin Oxide (ITO)-modified surface a quenching study was designed to capture the flip-flop dynamics in SLBs. The surface of ITO is dramatically changing the average lifetime of the fluorescent dyes, so that the lifetime gets shorter in proximity of ITO.

The effect is particularly noticeable within a few nm from the ITO surface. Such a distance matches well the thickness of the lipid bilayer. As a result the average lifetime of the dye in the inner leaflet is shortened in comparison to the average lifetime of the dye in the outer leaflet of the SLBs.

The bilayer was prepared from DOPC/DOPS (4:1) Small Unilamellar Vesicles (SUVs). The fluorescent dye (Flavone F2N12S) was added to the preformed SLBs. We followed the flipflop dynamics by monitoring the time evolution of the lifetime distribution after the addition of the dye.