

***1st Forum of Young Researchers on
Heterogeneous Catalysis***

BOOK OF ABSTRACTS

YOURHETCAT 2022

11 – 13th of July, 2022

Szeged, Hungary

1st Forum of Young Researchers on Heterogeneous Catalysis

Fighting climate change, most industrial technologies will not work without heterogeneous catalytic reactions. Understanding the catalytic processes, transferring and developing knowledge is essential. The 1st Forum of Young Researchers on Heterogeneous Catalysis 2022 (YOURHETCAT 2022) will be organized in Szeged, Hungary on July 11-13, 2022, hosted by **the Hungarian Catalysis Society (HCS)** with the help of **The Secretariat of the Regional Committees of the Hungarian Academy of Sciences at Szeged (MTA SZAB)** and the **European Federation of Catalysis Societies (EFCATS)**.

Our main goal is to support and link talented young researchers working in the field of catalysis by organizing a high-quality international event for free of charge without any registration fees. We are waiting for Graduated and Postgraduated Students, Postdocs as well as Senior Researchers of National and **European Catalytic Societies** and **the Young European Catalysis Network (YEuCAT)**.

The pre-planned program including 4-8 plenary lectures, 30-50 student presentations, 30-40 posters for the poster session and an extraordinary “pitch” presentation by 6-8 brave students, a tour of Szeged, coffee breaks, dinners and a lunch. We are expecting ~80 young researchers and more Senior Researchers from all over Europe, trusting in the exchange of experience, knowledge transfer and the creation of new cooperation opportunities, building networks, which will lead to the strong connection of International catalysis research.

Best wishes for all Colleagues by the Organizing Committee,

András Sápi – Szeged

József S. Pap – Budapest

Andrea Beck – Budapest

Ágnes Filep – Szeged

Nóra Győrffy - Budapest

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PLENARY LECTURES

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Fundamental aspects of ionic liquid interfaces

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Abstract

Ionic liquids (ILs) are salts with melting points below 100 °C. Typically, they are characterized by an extremely low vapour pressure. Since their physical and chemical properties can be tailored over a wide range, they represent a fascinating class of liquid materials with interesting applications in catalysis. Two important concepts in this context are Supported Ionic Liquid Phase (SILP) and Solid Catalyst with Ionic Liquid Layer (SCILL). In both, a high surface area solid substrate is covered with a thin IL film. In SILP, the film contains a homogeneously dissolved transition metal complex; in SCILL, the film modifies catalytically active surface sites at the support. The interfaces of the IL with the gas phase and with catalytic nanoparticles and/or support materials are thus of critical importance. These interfaces can be investigated in great detail under well-defined ultrahigh vacuum conditions using surface science methods like angle-resolved XPS, STM and AFM, along with in situ deposition of ultrathin IL films on solid supports. Not only information on the surface and bulk composition of non-functionalized and functionalized IL films or the reactivity of catalytically active metal complexes in ILs can be deduced, but also their interfaces can be studied on the molecular level. The obtained information includes the adsorption geometry and growth mode of IL on various support materials. A number of examples will be discussed.

Keywords: Ionic Liquids, SIPL, SCILL, adsorption, photoelectron spectroscopy, STM, AFM



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MoSe₂ - a versatile transition metal dichalcogenide and heterostructures thereof for applications in catalysis and optoelectronics

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Abstract

2D nanomaterials are an exciting class of materials in themselves amongst the nanomaterials. The sheer nature of these materials being confined along one dimension and with a huge surface area in the other two dimensions leads to very exciting properties. Transition metal dichalcogenide (TMD) nanosheets with defect-rich and vertically aligned edges are highly advantageous for various catalytic applications. Synthesis of TMDs using the colloidal techniques opens various possibilities to tune the electronic and optical properties of these 2D materials. As an example, we choose MoSe₂ nanosheets that have plenty of defects. The defect sites are responsible for adsorption on the surface thereby yielding excellent electrocatalytic hydrogen evolution and other catalytic activities on the surface. Further, these defects can be employed as seeding points to grow other materials on them. Cu₂S in these defect sites leads to a Type-II semiconductor heterojunction that allows for charge separation and therefore the MoSe₂-Cu₂S forms a superior material for generation of photocurrent and water splitting. Now even heterojunctions of MoSe₂, a hexagonal crystal with CsPbBr₃ – a perovskite have been enabled by use of a linker molecule 4 – aminothiophenol. Enhanced photocurrents are obtained with such a nanoheterostructure. This methodology further opens up avenues for forming heterostructures with large lattice mismatches and can therefore be of great potential use. Another method to explore heterostructures is to use two materials that form nanosheets and therefore are capable of coming close by means of van der Waals interactions. MoSe₂-SnS is one such nanoheterostructure that we have also fabricated.

Keywords: transition metal dichalcogenides, water splitting, HER, OER, photocurrent



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Operando Studies of Catalytic Surface Reactions

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Abstract

Operando characterization of working catalysts, requiring the simultaneous measurement of catalytic performance, is crucial to identify the relevant catalyst structure/composition and how molecules interact with interfaces [1]. Three examples illustrate what can be learnt from area-averaging and locally-resolved measurements.

i) *Area-averaging operando spectroscopy*: CO oxidation on Pt/ZrO₂ prepared by atomic layer deposition (ALD) was examined by sum frequency generation (SFG) spectroscopy and near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS), combined with mass spectrometry (MS) [2]. Complemented by Density Functional Theory (DFT), we show that the reaction onset is determined by a delicate balance between CO disproportionation (Boudouard reaction) and oxidation.

ii) *Spatially-resolved operando microscopy*: A combined photoemission electron microscopy (PEEM) and DFT study of supported meso-scale Pd particles demonstrates how a minute fraction of sites at the perimeter of the metal-oxide interface affects the CO oxidation performance of an entire Pd aggregate [3]. The initiation of CO-poisoning fronts is visualized at the perimeter, at a CO pressure two times higher for oxide-supported Pd aggregates than for unsupported ones. DFT calculations reveal stronger oxygen binding at the perimeter sites, explaining the higher CO-tolerance. As long as catalyst deactivation is not initiated, metal sites on oxide-supported Pd particles that are as far as several tens of μm away from the metal-oxide boundary maintain high catalytic activity even at increased CO pressure.

iii) *Single particle catalysis*: Using the apex of a Rh-nanotip as model of a single catalytic particle and field emission microscopy (FEM) as imaging tool, ongoing catalytic reactions can be visualized on the nm-scale [4]. Novel effects were revealed for H₂ oxidation, such as multifrequential oscillations on the nanoscale and limited interfacet coupling. Using ionized water as imaging species, the active sites were directly imaged by field ion microscopy (FIM). Local nano-pacemakers [5] were identified as being surface atomic configurations at the border between strongly corrugated Rh{973} regions and adjacent atomically flat terraces.

The insights by monitoring *ongoing* reactions may stimulate new ways of catalyst design.

Keywords: *operando, sum frequency generation, photoelectron spectroscopy, photoemission electron microscopy, field emission microscopy*

References

1. G. Rupprechter, Small (2021) 2004289
2. V. Pramhaas et al., ACS Catalysis 11 (2021) 208–214
3. Y. Suchorski et al., Nature Materials 17 (2018) 519–522
4. Y. Suchorski et al., Science 372 (2021) 1314–1318
5. J. Zeininger et al., ACS Catalysis 11 (2021) 10020–10027

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Simulations in electrocatalytic reduction of CO₂

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Abstract

CO₂ reduction with renewable energies opens the path to close the carbon cycle. Simulations have provided relevant insight on some important aspects of the materials under true reaction conditions. The materials under reaction conditions reconstruct and rearrange very extensively, these can be understood via the simulations as the direct observation is sometimes extremely challenging. Moreover, the electrolyte contributes to the overall activity and selectivity but the intimate mechanisms are still under debate. Finally, in many cases the activity towards compounds with more than two carbon atoms is limited to the use of copper. However, over the last years we have devised alternative materials that can break the copper limits.



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Photocatalysts for water pollution prevention

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Abstract

Plasmonic metals (Au, Ag) have an extremely large absorption/scattering cross-sections in the visible range and the ability to strongly focus light close to their surface. Therefore, they can offer new opportunities to overcome the limited efficiency of TiO_2 for utilizing it in various solar conversion devices such as photocatalysts and photovoltaic cells [1]. The underlying physical phenomenon for improved visible-light interaction is based on surface plasmon resonance (SPR). SPR helps in generating electrons and holes. It has been widely recognized that the hot electrons originate from the decay of the SPR and can be injected into the conduction band of TiO_2 , known as the hot electron injection process [2]. Thus, combining the plasmonic metals with TiO_2 can enhance the light interaction of TiO_2 through scattering, absorption, sensitization and hot electron injection [3]. The plasmonic metals not only improve the photo-absorption via SPR, but also provide a Schottky barrier (SB) at the interface between the metal and the semiconductor. This SB can induce excellent charge separation in such nanostructures. The Schottky barrier height (SBH) has been suggested to be an important parameter influencing the efficiency of the plasmon induced electron injection at the metal/semiconductor interfaces [4].

We fabricated novel multi-segmented Au/ TiO_2 NRAs as a representative example for investigating the harvesting of visible light, determination of the SB, and enhancement in photoelectron generation. The TiO_2 and Au/ TiO_2 nanorod arrays (NRAs) were fabricated by means of the template-assisted electrodeposition technique into anodic aluminum oxide (AAO) membranes. The XRD patterns of TiO_2 and Au/ TiO_2 NRAs confirm that TiO_2 is present in an amorphous form. This is favourable because the work function of amorphous TiO_2 is lower due to the large number of oxygen vacancies.

UV-Vis DR spectra for the free-standing NRAs show, for pristine TiO_2 , strong absorption in the UV range, and for Au/ TiO_2 sample a stronger absorption in the whole visible region (Fig. 2). In Au/ TiO_2 NRAs the broad peak at around 550 nm is associated with the transverse mode (T-mode) and another hump extends to the near IR region, which can be attributed to the longitudinal mode (L-mode) of Au NRAs. This indicates that the Au/ TiO_2 NRAs exhibit plasmonic behaviour under visible-light irradiation. The T-mode perfectly matches with the discrete dipole approximation (DDA) simulation data. However, the strong peak for the L-mode is less expressed. The latter is significantly affected by a change in Au segment lengths, presence of TiO_2 segments and the arrangement of Au NRAs, which can result in broadening and intensity loss of the L-mode. The plasmonic resonance energy transfer

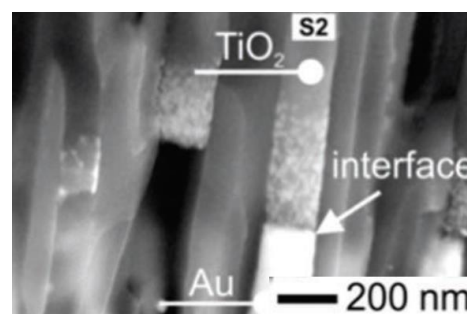


Fig. 1. SEM image of the multi-segmented Au/ TiO_2 NRAs embedded inside the AAO membrane.

(PRET) enhancement is dominant at the extremities of the Au segment, which penetrates into the TiO₂ segment for about 2 nm and creates a pathway for hot electron injection.

XPS analysis shows that Au in the Au/TiO₂ NRAs is negatively charged due to the electron transfer from oxygen vacancies in TiO₂ to achieve Fermi level equilibrium. This is due to the formation of the SB at the interface between Au and TiO₂. The valence band maximum (VBM) of Au/TiO₂ shifts towards a lower binding energy by 0.23 eV compared to pristine TiO₂ NRAs [5]. Finally, photoelectrochemical cell (PEC) measurements (Fig. 3) showed that the photocurrent density of Au/TiO₂ NRAs is 4 times larger than that of the pristine TiO₂, which is associated with the plasmon-sensitized process via hot electron injection and PRET enhancement from Au to TiO₂ segments. Obviously, the synergistic effect of the local PRET enhancement and the hot electron injection significantly increases the electron/hole pair generation in multi-segmented Au/TiO₂ NRAs.

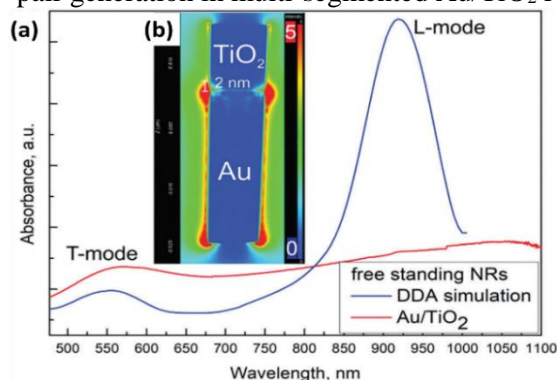


Fig. 2. (a) Comparison between UV-Vis DR spectra of Au/TiO₂ and DDA simulation on Au NR. (b) Enhancement in electric field intensity for a multi-segmented Au/TiO₂ NR.

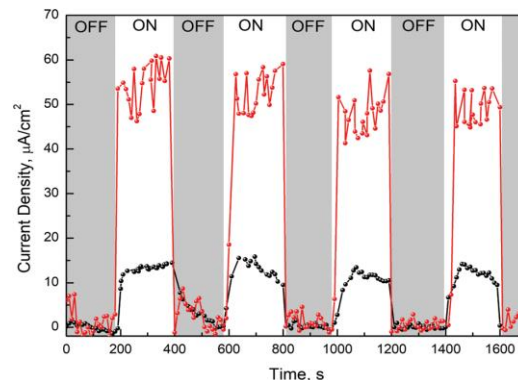


Fig. 3. Photoinduced current measurements on pure TiO₂ NRAs (black line) and multi-segmented Au/TiO₂ NRAs (red line) with and without light excitations

The same phenomena were recently demonstrated to occur as well in the presence of Au/TiO₂ nanorod particles [6,7]. By systematically synthesized Au/TiO₂ nanorods with different Au loadings, where the morphological, structural and surface properties of TiO₂ support were kept constant, it was confirmed that the rate of a photocatalytic reaction is directly influenced by the height of Schottky barrier (Fig. 4). It was proved that the SB height decreases and the extent of SPR effect increases with increasing the diameter/amount of Au ensembles on the catalyst surface, and that both properties are essential to obtain high visible-light triggered catalytic activity of Au/TiO₂ catalysts.

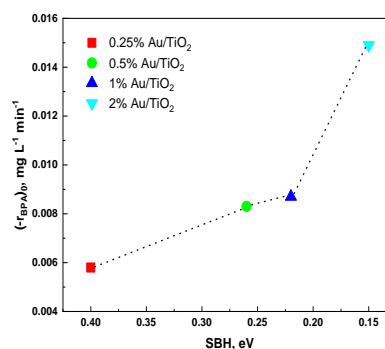


Fig. 4. Initial disappearance rate of water-dissolved bisphenol A (BPA) as a function of SBH obtained during the visible-light triggered photocatalytic degradation conducted in the presence of Au/TiO₂ solids. Operating conditions: V=250 ml, c₀=10.0 mg/l, T=25°C, c_{cat}=125 mg/l.

Acknowledgements - The financial support from the Slovenian Research Agency (research core funding No. P2-0150) is acknowledged.

References

- [1] Z. Xuming, C. Yu Lim, L. Ru-Shi, T. Din Ping, Rep. Prog. Phys. 76 (2013) 046401.
- [2] X.-C. Ma, Y. Dai, L. Yu, B.-B. Huang, Light: Sci. Appl. 5 (2016) 16017.
- [3] W. Hou, S.B. Cronin, Adv. Funct. Mater. 23 (2013) 1612.
- [4] M.R. Khan, T.W. Chuan, A. Yousuf, M.N.K. Chowdhury, C.K. Cheng, Catal. Sci. Technol. 5 (2015) 2522.
- [5] M.S. Arshad, Š. Trafela, K. Žužek Rožman, J. Kovač, P. Djinović, A. Pintar, J. Mater. Chem. C 5 (2017) 10509.
- [6] G. Žerjav, J. Zavašnik, J. Kovač, A. Pintar, Appl. Surf. Sci. 543 (2021) 148799.
- [7] G. Žerjav, M. Roškarič, J. Zavašnik, J. Kovač, A. Pintar, Appl. Surf. Sci. 579 (2022) 152196.

POSTER AND ORAL CONTRIBUTIONS

*(the abstracts are arranged in the alphabetical order of the
name of the presenting authors)*

Solvent-Free Synthesis, In Vitro and In Silico Studies of Novel Potential 1,3,4-Thiadiazole-Based Molecules against Microbial Pathogens

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Abstract

A new series of 1,3,4-thiadiazoles was synthesized by the reaction of methyl 2-(4-hydroxy-3-methoxybenzylidene) hydrazine-1-carbodithioate (2) with selected derivatives of hydrazonoyl halide by grinding method at room temperature. The chemical structures of the newly synthesized derivatives were resolved from correct spectral and microanalytical data. Moreover, all synthesized compounds were screened for their antimicrobial activities using *Escherichia coli*, *Pseudomonas aeruginosa*, *Proteus vulgaris*, *Bacillus subtilis*, *Staphylococcus aureus*, and *Candida albicans*. However, compounds 3 and 5 showed significant antimicrobial activity against all tested microorganisms. The other prepared compounds exhibited either only antimicrobial activity against Gram-positive bacteria like compounds 4 and 6, or only antifungal activity like compound 7. A molecular docking study of the compounds was performed against two important microbial enzymes: tyrosyl-tRNA synthetase (TyrRS) and N-myristoyl transferase (Nmt). The tested compounds showed variety in binding poses and interactions. However, compound 3 showed the best interactions in terms of number of hydrogen bonds, and the lowest affinity binding energy (-8.4 and -9.1 kcal/mol, respectively). From the in vitro and in silico studies, compound 3 is a good candidate for the next steps of the drug development process as an antimicrobial drug.

Keywords: Grindstone chemistry, 1,3,4-Thiadiazoles, antimicrobial, MIC

Characterization and evaluation of photocatalytic activity of strontium titanate photocatalyst prepared by different synthesis methods

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Abstract

Strontium titanate (SrTiO₃) photocatalysts were prepared using hydrothermal, sol–gel, and co-precipitation methods. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), infrared spectroscopy (IR), diffuse reflectance spectroscopy (DRS), and nitrogen adsorption/desorption (BET) measurements. The photocatalytic activity of the samples was evaluated by the photocatalytic oxidation of phenol and oxalic acid under UV light irradiation. Their photoactivity was compared to a commercially available SrTiO₃ photocatalyst used as a reference. The causal relationship between the morpho-structural properties and photocatalytic activity was also investigated. Based on the XRD results, sol–gel and hydrothermal methods resulted in pure SrTiO₃; however, the sample obtained using the co-precipitation method contained impurities. It was found that the concentration of citric acid used during the sol–gel synthesis had a profound effect on the efficiency of the photocatalysts: lower citric acid concentration resulted in higher photoactivity. Our homemade SrTiO₃ photocatalysts had higher photocatalytic activity than that of the commercial SrTiO₃ reference in most cases. Homemade SrTiO₃ prepared at the lowest citric acid concentration led to the best photocatalytic degradation results for both phenol and oxalic acid. This result is in good agreement with those of the DRS measurements: the best performing sample had the narrowest band gap resulting in its most efficient excitation.

Keywords: Strontium titanate, Oxalic acid, Phenol, Citric acid, Photocatalysis

Density functional theory and STM simulation study of nitrogen-doped graphene configurations on Ir(111) and Ru(0001) surfaces

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Abstract

Currently, there is much economic and ecological pressure for viable new metal-free catalysts for new technologies. Nitrogen-doped graphene has shown itself to be a powerful alternative with potential uses that can go from the fuel cells to electrochemical biosensing, comparable in efficiency to the current Platinum-based catalysts. A multitude of possible doping structures for the nitrogen on graphene (graphitic, pyridinic, pyrrolic, etc.) have different effects on catalysis, and a better understanding of the formation and atomic-scale detection of such defects is fundamental for further development in this area. For such, we employ density functional theory (DFT) calculations of corrugated N-doped graphene single layers over two different substrates: Iridium(111) and Ruthenium(0001). Considering systematically selected N-doped graphene defect configurations, their energetic preference is correlated with their atomic structure. Scanning tunneling microscopy (STM) simulations going beyond the Tersoff-Hamann (spherical tip orbital) model were performed, and a great variety of STM image contrasts showed good agreement in comparison with experimental STM images. This work provides further insight into the structure and bonding configuration of N-doped graphene in its different configurations, and will certainly be helpful to design a vast array of cheaper, more efficient, and more eco-friendly devices in the future.

Keywords: nitrogen doping, graphene, iridium, ruthenium, DFT, STM

Investigation of TiO₂-based Ru, Rh, Pt metal catalysts in photocatalytic CO₂ hydrogenation reactions

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Abstract

In this work the performance of TiO₂ and TiO₂ based Ru, Rh and Pt metal catalysts are investigated in photocatalytic CO₂ hydrogenation reactions with particular reference to the selectivity and conversion to CO. TiO₂ is one of the most widely used material in photocatalytic reactions. However, the pure TiO₂ showed less CO conversion, this particular trait has to be enhanced with precious metals. The catalysts were prepared by wet impregnation of Ru, Rh and Pt salts on the surface of anatase, with 1wt% of each noble metal. The samples characterized using UV-Visible diffuse reflectance spectroscopy, X-ray diffractometry (XRD) and transmission electron microscopy (TEM). The experiments were carried out using an UV-photoreactor connected gas chromatograph (GC), and the results have shown that the noble metals changed the photocatalytic activity of the TiO₂ in a positive way. Specifically, Rh/TiO₂ has the highest conversion rate (up to 12%). In regards of selectivity, all samples are highly selective to CO.

Keywords: CO₂ hydrogenation, photocatalysis, titanium dioxide, precious metals

Nitrogen doped carbonaceous materials as platinum free cathode electrocatalysts for oxygen reduction reaction

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Abstract

Polymer Electrolyte Membrane Fuel Cells (PEMFCs) are feasible power sources to generate electricity by converting chemical energy of H₂ into electrical one directly with its several pros, such as high efficiency, low operating temperature, and low emission of greenhouse gases. Since one of the principal components of PEMFCs are Pt-based electrocatalysts supported on carbon, reducing the amount of platinum used (up to zero) remains one of the main directions of studies. Recent reports revealed that various types of carbon nanostructures doped with non-metal such as B, P, S and especially N have a high potential for oxygen reduction reaction (ORR)^{1,2} occurring on the cathode side of PEMFCs. Presence of N in graphene oxide (GO)/ graphene plane was found to enhance the ORR activity and to promote the favorable four-electron process for the ORR.²

In this study, 3 different N-doped carbonaceous materials were prepared to compare their ORR activity: N-doped GO (N-GO), N-doped graphene nanoplatelets (N-GNP), synthesized by solvothermal synthesis, and N-doped multilayer graphene (N-Gr) obtained by ball-milling from graphite and melamine. For characterization of the samples XRD, XPS, nitrogen adsorption, Raman spectroscopic, microanalytical analyses, cyclic voltammetry and rotating disc electrode (RDE) technique were performed. The obtained samples differed both in the distribution of N-functional groups (N_{pyridic}, N_{pyrrolic}, N_{pyridic NO}, N_{quaternary}) and in the surface nitrogen content, which decreased in the following order: N-Gr (14%)>N-GO (7%)>N-GNP (3%). An attempt was made to find relationship between the structural features and electrocatalytic behavior, which will be discussed in the lecture.

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References:

1. Duo Wu, W. & Xu, D. *Electrocatal. Fuel Cells Hydrog. Evol. - Theory to Des.* (2018) doi:10.5772/intechopen.77048.
2. Ikeda, T. et al. *J. Phys. Chem. C* 112, 14706–14709 (2008).

Keywords: nitrogen-doped carbon, oxygen reduction reaction, PEMFC, cathode catalyst

Study of the Photoelectrochemical Hydrogen Evolution Reaction on Exfoliated SnSe Electrodes

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Abstract

Photoelectrochemical hydrogen evolution reaction (PEC HER) is one of the most promising methods to achieve solar-to-hydrogen conversion. Tin selenide (SnSe) is an excellent candidate for PEC HER due to its suitable conduction band position to drive the water reduction process and high absorption coefficient to absorb solar energy. Liquid phase exfoliation (LPE) method is one of the most applied approaches to produce suspension of nanoflakes from its bulk counterpart with low-cost and high yield. In this study, LPE was applied to prepare SnSe nanoflakes in different solvents, namely the mixture of IPA/H₂O with different IPA contents. The PEC activity of SnSe nanoflakes was increased with the rising IPA content and the pure IPA produced SnSe nanoflakes exhibited 10 times higher activity than that made in the mixture of IPA/H₂O. Additionally, a sieving system was used to separate as-received SnSe crystals to different sizes prior to LPE process, which further improved the PEC performance of SnSe electrodes. The electrodes prepared by the largest size SnSe crystal exfoliated in IPA showed the highest photocurrent of $3.17 \pm 0.42 \text{ mA cm}^{-2}$ at -0.74 V versus RHE. This demonstrates about 3-times higher PEC performance compared with previous results in the literature. The existence of SnSe₂ phase in SnSe samples was proved by Raman spectroscopy and X-ray diffraction, and the percentage of SnSe₂ raised as the decrease of initially used SnSe crystal-size. These results indicate the applicability of SnSe electrodes in PEC HER, and inspire us to explore other photoelectrocatalytic reactions on the exfoliated SnSe.

Keywords: liquid phase exfoliation, semiconductor, PEC activity, size-control

Turning CO₂ to CH₄ and CO over CeO₂ and MCF-17 supported Pt, Ru and Rh nanoclusters – Influence of nanostructure morphology, supporting materials and operating conditions

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Abstract

Efficient conversion of CO₂ into CH₄ and CO brings an important opportunity to get valuable feedstock for a variety of industrially important reactions as both CH₄ and CO are widely used as starting materials for the synthesis of valuable fuels and chemicals. Herein, we synthesized sub-nanometer (<2nm) Platinum (Pt), Ruthenium (Ru) and Rhodium (Rh) nanoclusters (NCs) via colloidal method; successfully decorated over mesoporous CeO₂ and high surface area (HSA) siliceous meso-cellular foam (MCF 17) and tested for high-pressure CO₂ reduction at lower temperature range (220–340 °C). Pt and Ru NCs exhibited typical reverse water gas shift (RWGS) and methanation catalytic performance, respectively, with minimal influence of the nature of support. However, Rh NCs showed drastic variations in the product selectivity, which exhibited strong influence of the support over the product distribution. Furthermore, Ru NCs (with a relatively lower metal loading ~ 1 wt %) were found to be highly selective to CH₄ (~99 %) and stable (up to 40 hr time on stream) with either CeO₂/MCF 17 at 340 °C; also, Ru NCs exhibited comparatively the highest CO₂ conversion (~93 % in case of Ru NCs/CeO₂) among the supported metal NCs. HRTEM results showed that metal NCs were homogeneously dispersed with a controlled and uniform particle size (<2nm); no substantial agglomeration of Ru NCs were observed after reaction. Beside the stable dispersion of NCs, Near Ambient Pressure (NAP) in situ XPS of Ru/CeO₂ showed that the dynamic Ce³⁺/Ce⁴⁺ ratio of CeO₂ can attribute to the high activity and selectivity.

Keywords: sub-nanometer (<2nm), CO₂ activation, NAP-XPS

Carbon Dioxide Photocatalytic Hydrogenation using ZnO/Fe₂O₃

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Abstract

Global warming is a big challenge for humanity and CO₂ emission is the main problem. So recycling carbon dioxide to added value hydrocarbon is one of the solutions. In this research CO₂ has been photocatalytic hydrogenated using ZnO/Fe₂O₃ synthesized by hydrothermal method with different iron concentrations. The samples were characterized using X-ray diffraction (XRD) and UV-visible reflectance spectroscopy. The CO₂ hydrogenation was taken place in a glass photoreactor in batch mode using UV lamp. The XRD revealed formation of single phase of hexagonal ZnO and UV-visible spectroscopy determined the maximum absorption and the band gap were calculated. The photocatalytic test results showed 22% and 8% conversion with 100 and 99% selectivity with 1.5 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ and 1 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ CO for ZnO/Fe₂O₃ and pure ZnO respectively.

Keywords: Photocatalysis, Hydrogenation, Band gap.

Acid-base reactions of acetaldehyde on modified Rh(111) surfaces

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Abstract

The adsorption and reactions of acetaldehydes (AA) has been studied on clean and modified Rh(111) single crystal surfaces by standard UHV methods, such as TDS and HREELS. In this work we are going to compare the effects of two type of surface additives - oxygen and potassium – on the reactions of AA. In our previous works we found that 1.) preadsorbed oxygen may interact with HCOOH and H₂CO so increasing the formation of surface formate [1] as well as 2.) the presence of K atom enhances the adsorption of formic acid and stabilize the HCOO groups by direct and through space electronic effects. On bare rhodium surface acetaldehyde adsorbs in h¹-CH₃CHO_a and h²-CH₃CHO_a. In the adsorbed layer further reactions like formation of oligomers, decomposition and finally the release of AA, oligomers, CO, H₂, CH₄ were observed by mass spectrometry [2]. In the case of preadsorbed oxygen the CH₃CHO molecules were transferred to acetate. This was confirmed by HREELS as these adsorbed forms have a characteristic ν_a(OCO) vibration at 1660 cm⁻¹ which was present up to T=325 K. The adsorbed layer readily decomposes to H₂O, CO₂ and CH₃COOH. Potassium atoms dramatically changed the stability of AA molecules. Thermal desorption spectra taken from the coadsorbed layer show large shifts in the corresponding peaks of CH₄, CO. For H₂ desorption at T=395 K and T=596 K. This finding was supported by the HREELS peaks at 1810-2100 cm⁻¹. When interpreting these results we may consider the tautomeric rearrangement of the AA molecule.

References:

1. Imre Kovács, János Kiss, Frigyes Solymosi; Vacuum 138 (2017) 152 -156
2. Imre Kovács, Arnold Péter Farkas, Ádám Szitás, Zoltán Kónya, János Kiss; Surface Science 664 (2017) 129–136

Keywords: TDS, potassium, oligomer, HREELS

Fabricating Quercetin arbitrated efficient visible light driven bismuth oxybromide/bismuth oxyiodide [BiOBrpI1-p-Q] facilitated by defect Engineering via simple mechanical grinding: An Experimental and DFT insight

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Abstract

Bismuth oxyhalides fabricated via grinding have shown promising photocatalytic activity under visible light irradiation. Bismuth oxybromide and bismuth oxyiodide composites were successfully fabricated using green solvent free simple mechanical grinding technique using Quercetin (Q) as reducing sensitizer. The concentration of oxyhalides were varied from 0.2-0.8 viz. BiOBrpI1-p-Q (p=0.2, 0.4, 0.5, 0.6, 0.8). The synthesized photocatalysts were used to degrade Methyl Orange (MO) and Phenol (Ph) and the best activity was found of BiOBr0.8I0.2Q heterostructure. The fabricated heterostructures were endowed with oxygen rich vacancies within 15 minutes of fabrication time. During fabrication, Quercetin was able to grow on p type BiOBr and n type BiOI due to presence of positively charged Bi(III) ions and negatively charged Oxygen ions of Q, respectively. The formation of pn junction was confirmed by Mott-Schottky plot. Significantly, the Q was not only able to reduce BiOBr and BiOI but was also able to create oxygen rich vacancies, which effectually improved visible light adsorption as well as charge separation efficiency. Owing to synergistic effect of formation of pn junction and oxygen vacancies, higher photogenerated charge carriers and reactive oxygen species were present for photodegradation of MO and Ph, respectively. The photocatalytic efficiency was significantly convalesced from pristine BiOBr and BiOI. The Density Functional Theory (DFT) based calculations were performed for pristine BiOBr, BiOI as well as BiOBrpI1-p-Q with oxygen vacancies, that provided an insightful understanding of the pn junction formation, effect of oxygen vacancies, physical mechanism, and superior photocatalytic performance of BiOBr0.8I0.2Q heterostructure over other samples.

Keywords: Density functional theory; p-n heterojunction; phenol degradation; green grinding synthesis; oxygen vacancies

Evaluation of graphene role on the photocatalytic properties of copper oxides/graphene/TiO₂ nanoparticles composites

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Abstract

Easy and cost-efficient modifications of titanium dioxide nanoparticles that improve their efficiency in the visible light domain represent a continuous and challenging research topic. In addition, the effect of graphene on the overall photocatalytic process is still unclear.

Consequently, herein we prepared a series of TiO₂ nanoparticles-based composites with different copper oxides mass content (1-3%) and co-doped with graphene of different oxidation degrees. Different characterization techniques were used to analyze the structural and physicochemical properties of the obtained composites: SEM/TEM/EDX microscopy, XRD, FT-IR and XPS spectroscopy. The photocatalytic performance has been evaluated by the degradation of methylene blue under both UVA, or visible light irradiation. The nanocomposites show very good photocatalytic activity independent on the presence of reduced graphene oxide, due to the Cu₂O/CuO-TiO₂ heterojunctions. This finding has been further confirmed by the very efficient visible light-driven degradation of amoxicillin and ciprofloxacin.

Keywords: *copper oxides-TiO₂-graphene composite; methylene blue UVA photodegradation; Cu₂O/CuO-TiO₂ heterojunction; Titanium dioxide nanoparticles (TiO₂)*

Structure-catalytic activity correlations of Pt/m-MnO₂ system in CO₂ hydrogenation

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Abstract

The investigation of the surface structure and active centers of a catalyst under relevant reaction conditions is crucial for the elucidating of structure-catalytic activity correlations. The deposition of controlled size 0.5% Pt nanoparticles onto the mesoporous MnO₂ greatly enhances the catalyst's turnover in the ambient pressure CO₂ hydrogenation. At the same time, no selectivity change was registered: both mesoporous MnO₂ (m-MnO₂) and Pt supported m-MnO₂ (Pt/m-MnO₂) exhibited ~100% CO selectivity. This work aims at understanding the Pt-Manganese-Oxide surface interaction responsible for the improved catalytic performance. NAP-XPS results clarify that under reaction conditions the active phase of Platinum is metallic while manganese predominantly can be found as MnO. In contrast, for pure support, Mn³⁺ was mostly detected in the surface layer. In this regard, identical reaction conditions were implemented to probe commercial irreducible Mn(II)O and its 0.5% Pt-loaded counterpart. The same trend in activity was observed, which further confirms beneficial synergy between MnO and Pt nanoparticles. In-situ DRIFTS revealed weakly adsorbed CO band that appeared on Pt/m-MnO₂ at a low wavenumber (at 2020 cm⁻¹) and was attributed to CO perturbed by hydrogen (HCO). These species were not registered on other Pt nanoparticles supported mesoporous metal oxides. In order to investigate the structure, HR-TEM analysis was performed over spent Pt/m-MnO₂. Clear edge dislocations were found at the Pt-MnO interface. Combining these results with further spectroscopic measurements and CO₂-TPD analysis, it was proposed that lattice mismatch at the Pt-MnO interface is favorable site for the generation of HCO species, which are active in the producing of CO.

Keywords: CO₂ hydrogenation, MnO₂, XRS, DRIFTS, HR-TEM

Black titania nanotubes/spongy graphene nanocomposites for high-performance supercapacitors

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Abstract

A simple method is demonstrated to prepare functionalized spongy graphene/hydrogenated titanium dioxide (FG-HTiO₂) nanocomposites as interconnected, porous 3-dimensional (3D) network crinkly sheets. Such a 3D network structure provides better contact at the electrode/electrolyte interface and facilitates the charge transfer kinetics. The fabricated FG-HTiO₂ was characterized by X-ray diffraction (XRD), FTIR, scanning electron microscopy (FESEM), Raman spectroscopy, thermogravimetric analysis (TGA), UV-Vis absorption spectroscopy, and transmission electron microscopy (TEM). The synthesized materials have been evaluated as supercapacitor materials in 0.5 M H₂SO₄ using cyclic voltammetry (CV) at different potential scan rates, and galvanostatic charge/discharge tests at different current densities. The FG-HTiO₂ electrodes showed a maximum specific capacitance of 401 F g⁻¹ at a scan rate of 1 mVs⁻¹ and exhibited excellent cycling retention of 102% after 1000 cycles at 100 mV s⁻¹. The energy density was 78.66 W h kg⁻¹ with a power density of 466.9 W kg⁻¹ at 0.8 A g⁻¹. The improved supercapacitor performance could be attributed to the spongy graphene structure, adenine functionalization, and hydrogenated titanium dioxide.

Keywords: Black titania, spongy graphene and supercapacitors

Antimicrobial and Photocatalytic degradation activities of Capsaicin coated Cobalt Ferrite Magnetic nanoparticles

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Abstract

In this study, CoFe₂O₄ nanoparticles were modified by Capsaicin extracted from hot pepper *Capsicum annuum* ssp. CoFe₂O₄ NPs were synthesized by coprecipitation method. The virgin CoFe₂O₄ NPs and Capsaicin-coated CoFe₂O₄ NPs (CPCF NPs) were characterized by XRD, FTIR, SEM, and TEM and their antimicrobial potential and photo-catalytic degradation of Fuchsine basic (FB) were investigated. CoFe₂O₄ NPs have spherical shape and their diameter varied from 18.0 nm to 30.0 nm with average particle size at 25.0 nm. Antimicrobial activity was tested towards gram positive (*S. aureus*) and gram negative (*E. coli*) as zone of inhibition (ZOI) and minimum inhibitory concentration (MIC). UV-assisted photocatalytic degradation of FB was investigated. Various parameters affecting the photocatalytic efficiency such as (pH, initial concentration of FB, and dose of nanocatalyst) were studied. The in-vitro ZOI and MIC result verified that CPCF NPs are also active upon Gram-Positive *S. aureus* (23.0 mm ZOI and 0.625 ug/ml MIC) than Gram-Negative *E. coli* (17.0 mm ZOI and 1.250 ug/ml MIC). Results obtained from the photocatalytic activity indicated that the maximum FB removal achieving 94.6% in equilibrium was observed using 20.0 mg of CPCF NPS at pH 9.0. The synthesized CPCF NPS are effective for the removal of FB and potent antimicrobial agent for both gram positive and gram negative bacteria with possible application in the wastewater treatment.

Keywords: Capsaicin, Magnetic nanoparticles, Antimicrobial activity and Photocatalysis.

Production of Biodiesel as Renewable Energy from Microalgae (*Chlorella* and *Micractinium*)

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Abstract

Fossil fuels are unsustainable because of their limited supplies, they cause global warming because of their CO₂ emissions. The main goal for this research is to produce Biofuel (Biodiesel) to find an alternative product which is renewable source, reduce CO₂ emissions that cause global warming so we will achieve the sustainable development goals (SDGs) and maintain green environment. The production of Biodiesel will be achieved by isolation microalgae from different sources, purification and identification of microalgae species (*Chlorella* and *Micractinium*), screening the ability of isolated species for lipid production, selecting the highest growth rate of algal species among the highest producing lipid ones, optimizing the different conditions of microalgae culturing then cultivating in laboratory and constructed a small open pond to maximize oil production, harvesting of algae by centrifugation, oil extraction to give the maximum quantity of oil to convert oil to biodiesel by transesterification process. Finally, assess fatty acid profile for algal oil using gas chromatographic analysis (GC) to determine biodiesel quality is proposed. *Chlorella* in control conditions gives 29.65% saturated fatty acids that will be converted to biodiesel and 65.5% unsaturated fatty acids that are used in medical application. While in the optimized condition, we noticed decrease in the saturated fatty acids to 25.7%, but we notice increase in the amount of poly unsaturated fatty acids to 56.2%. In regard to *Micractinium*, it gives 21.2% saturated fatty acids and it increased to 28% in the optimized conditions.

Keywords: Biodiesel production, Microalgae cultivation, FAME, Lipid enhancement, Transesterification

Synthesis of BN-Graphene hetero-monolayer via CVD in benzol-borazene gas mixture on Rh(111) surface

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Abstract

The development of CVD fabrication techniques of different 2D materials on transition metal surfaces is nowadays one of hot topics in the nanotechnology. These efforts are mainly due to the wide range of physical-chemical properties of the special 2D materials, accordingly, their extremely huge application potential both in nanochemistry and nanoelectronics. One of the crucial and usually determining properties is the bandgap (BG). From this point of view graphene and hexagonal boron-nitride (h-BN) stand at the two final points of the scale: the former one is a well known zero BG material, while h-BN is a 2D material with one of the highest BG value (around 6eV). Mainly because of their very similar ring morphology (lattice constant) and iso-electron configuration, it seems plausible that the high level mixing (formation of hexagon rings by all three elements B, C, N) of these two component can result in synthesis of new BCN materials with a huge variability of BG. Nevertheless, the low level mixing (connecting nanopatches of the two individual materials of graphene and h-BN) can also have several interesting properties. All these cases lead to an interesting topic of examination of hetero-nanostructure formation (both in horizontal or vertical mode).

This work is devoted to a morphological STM study of graphene/h-BN heteros formed on Rh(111) surface in high temperature CVD processes running in precursor gas phases of different benzene/borazin ratio.

Keywords: benzol-borazine gas mixture, CVD, $B_xC_yN_z$ 2D nanocomposit, Rh(111), STM-STs

Synthesis of MIL-53(Al)-based catalysts for the methanation of CO₂

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Abstract

Metal-organic frameworks (MOFs) are one of the most discussed classes of materials in the last decade. The particular interest in MOF materials in catalysis is due to their modularity, ultrahigh surface area, organic-inorganic hybrid composition, crystalline nature, and tunable porosity. To facilitate their use in various catalytic processes, it is desirable to develop new synthetic methodologies to obtain multifunctional MOF composites which exhibit enhanced properties to those of the individual components, especially enhanced thermal stability.

MIL-53(Al) is a microporous aluminium-based MOF best known for its flexible structure, as well as its excellent thermal stability. This work aims to report the synthesis and characterization of MIL-53(Al) and MIL-53(Al)-Al₂O₃ composite, and to evaluate their performance as catalytic supports in the methanation of CO₂. MIL-53(Al) and MIL-53(Al)-Al₂O₃ composite were synthesized under hydrothermal conditions from aluminium nitrate and alumina as metal sources with very good quality, as confirmed by powder X-ray diffraction, N₂ adsorption-desorption isotherms, and thermogravimetric analysis. The obtained MIL-53(Al) structures were used as catalytic supports for the deposition of Ni nanoparticles and their catalytic activity was tested in the methanation of CO₂ under temperature-programmed reaction and stability tests for 24 time on stream.

Keywords: MIL-53(Al)-Al₂O₃, Ni@MIL-53(Al) catalysts, CO₂ methanation

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Cobalt catalysts supported on SBA-15 and ZSM-5 for CO and VOCs oxidation

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Abstract

Abatement of volatile organic compounds (VOCs) in the waste gases is an important task in the areas of environmental protection. The European Commission presented the so-called Green Deal in December 2019, also known as the Green Pact, which is a set of policies aimed at making Europe climate neutral by 2050. The design of a catalytic system for complete oxidation of hydrocarbons is an important problem of the environmental catalysis. Cobalt oxide is reported as quite promising among the metal oxides used for preparation of supported catalysts for the removal of VOC's. The main drawback of the transition metal oxides catalysts is the deactivation as result of an aggregation. The problem could be tackled by application of supports with new properties, as those of nanostructured porous oxides. Zeolites are one such type of carrier because of their specific pore structure, acidic properties, high thermal stability and the ability to exchange ion. Another type of supports that science is increasingly interested in is mesoporous oxides such as SBA-15. This work is focused on the investigation of the structural and catalytic properties of mono component cobalt catalysts supported on SBA-15 and ZSM-5. Cobalt was incorporated from $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ by incipient wetness impregnation technique followed by drying and calcination. The obtained materials were characterized by XRD, TPR, and XPS and tested in complete oxidation of n-hexane and butane. Higher activity in both reaction is shown by the samples supported on ZSM-5, probably due to the presence of easily reducible phases.

Keywords: Co-SBA-15, Co-ZSM-5, n-hexane combustion, butane combustion

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Platinum modified Beta zeolite catalysts: a DFT study on metal sites formation and energetics

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Abstract

Zeolites, with their Brønsted acid sites and the microporous network of cages capable of hosting metal atoms, are extensively used as heterogeneous catalysts in several reactions of the refining industry, requiring metal-acid functionalities to improve fuels properties.

Upstream of any process study, catalyst tuning is needed, and quantum mechanical calculations can turn out essential, being well established the advantages of atomistic approaches on the design of catalysts and optimization of active sites.

In this context, periodic density functional theory was used to provide insights on the preferential location of a platinum atom encapsulated in Beta zeolite's cages. Cluster growth was subsequently addressed, up to Pt₃@BEA systems, following a one-by-one atom addition. An unbiased approach in making the initial guess for Pt_n (n=1-3) coordinates within the zeolite framework was employed. Thus, a wide panorama of structures being considered, the analysis was performed on energetics, cluster geometries and cavity distortions.

The optimal geometry of interaction for a single platinum atom involves two strong Pt-O bonds in linear arrangement, even with a distorted zeolite framework, a structure where a Si-O bond is broken to allow the formation of the nearly 180° angle. Zeolite breakage characterises also the stablest Pt₂ and Pt₃@BEA structures, the driving force for this occurrence being the same. Platinum migration is hindered by high energy barriers of ca. 100 kJ/mol. Energetic preference for Pt clustering is observed, with Pt₃ favoured with respect to 3Pt within the pure siliceous BEA framework.

Keywords: Zeolites, platinum, catalyst design, cluster growth, DFT

Modified layered double hydroxides for glucose-to-fructose selective isomerization

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Abstract

The development of selective and efficient catalysts to gain fuels and chemicals from renewable sources is a highly desired outcome of modern research efforts. Biomass with high cellulose content gives an excellent opportunity to obtain platform molecules such as 5-hydroxymethylfurfural (5-HMF) in an economically favorable way. Solvents, polymers, and potential biofuels can be produced from this platform molecule. Since the rate-determining step of the synthesis of 5-HMF from cellulose is the isomerization of glucose to fructose, our primary focus was on this step. As an expensive enzyme catalyst is used in the industry for this reaction, a new, selective heterogeneous catalyst can give a more efficient solution to the rapidly growing demand for fructose.

For this reason, we used and optimized members of the highly variable layered double hydroxides (LDHs) material family for glucose isomerization. It quickly became apparent that the synthesis method of the LDHs highly affected the ratio of the basic and acidic sites on the surface and thus the catalytic activity. We were able to fine-tune the surface basicity, the porosity and the composition. Using the optimal modifications of the catalyst, a selective reaction was obtained with almost total conversion under mild and environmentally friendly reaction conditions.

Keywords: glucose-to-fructose isomerization, structure-activity-stability relationship, selective catalytic transformation

Effect of Particle Size on Resistance to Chloride for Hydrodechlorination of Trichloroethylene in Water

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Abstract

Removal of trichloroethylene (TCE) from groundwater is crucial because it is an environmental hazard and worldwide drinking water demand is generally provided by groundwater. Hydrodechlorination (HDC) is a desirable catalytic approach for remediation of TCE. Pt/Pd-based catalysts show high catalytic activity for HDC. However, the catalytic performance is adversely affected by inhibition due to unavoidable reaction product HCl. The inability of HCl to desorb from the active sites leads to complete loss of the activity and irreversible catalyst deactivation by the chloride poisoning. This effect, however, could be alleviated by designing a catalytic system in which the inhibition reaction is suppressed. In this study, the objective is to investigate the effect of particle size of Pt nanoparticles on resistance to chloride poisoning for HDC of TCE in water. The study includes synthesizing Pt nanoparticles with three different particle size by colloidal synthesis method, performing activity experiments in a semi-batch reactor, carrying out characterization studies and performing kinetic measurements. The results demonstrate that desired Pt NPs were synthesized successfully as evidenced by transmission electron microscopy. The fastest reaction kinetics and highest resistance to chloride poisoning were observed at the smallest particle size. Kinetic experiments performed at different concentrations of TCE over the equal basis of Pt weight and the equal basis of Pt surface area revealed insight into structure sensitivity of reactions involved in HDC of TCE in water at atmospheric conditions.

Keywords: Hydrodechlorination, Trichloroethylene, Platinum, Nanoparticle, Catalysis

Preparation of inverse opals with different wall thickness by atomic layer deposition

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Abstract

TiO₂ based materials are intensely studied in the field of photocatalysis in all shapes and compositions.^[1] One of the vast structural options of TiO₂ based photocatalyst is the inverse opal, which has photonic capabilities. While TiO₂ photonic crystals have photocatalytic properties on their own, the addition of other elements, particles, ions can increase it.^[2] However, the modification of the inverse opal structure can have an effect on the photocatalytic efficiency on their own, due to the structural dependency of the photonic band gap. The pore size of the inverse opal depends on the size of the nanospheres used as in the template colloid crystal during the preparation, also more complex structures can be achieved using two nanospheres with different diameters.^[3,4]

In this study, the aim was to explore another possible way to alter photonic band gap structure of the inverse opal: with the partial infiltration of the opal template. We suspect that the insufficient filling of the template opal causes remnant cavities inside the inverse opal structure, which can alter the photonic band gap. The opal templates were made by vertical deposition technique from polystyrene (300 nm diameter) and carbon (458 nm diameter) nanospheres. The templates were coated with 16.5 nm, 34.3 nm and 49.7 nm TiO₂ layer by ALD, then the templates were removed by calcination, which resulted in six inverse opal samples. Characterization was done by SEM, EDX, XRD, DR UV-Vis and reflectance UV-Vis. Photocatalytic experiments were carried out by Raman spectroscopy and digital photography.

Keywords: inverse opal, atomic layer deposition, photocatalysis

References:

- [1] K. Nakata, A. Fujishima, J. Photochem, C. Photobiol, Photochem. Rev., 13 (2012), pp. 169-189
- [2] J. Yu, J.Y. Lei, L.Z. Wang, J.L. Zhang, Y.D. Liu, J. Alloys Compd., 769 (2018), pp. 740-757
- [3] Rick C. Schroden, Mohammed Al-Daous, Christopher F. Blanford, and Andreas Stein, *Chem. Mater.* 2002, 14, 8, 3305–3315
- [4] Zhongyu Cai, Jinghua Teng, Zhigang Xiong, Yanqiang Li, Qin Li, Xianmao Lu, and X. S. Zhao, *Langmuir* 2011 27 (8), 5157-5164

Methanation of CO₂ using MOF(Al)-derived Ni catalysts

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Abstract

Metal-organic frameworks (MOFs) are very appealing materials due to their exceptional properties such as tunable porous structure, high surface area, and structural diversity, especially for gas sorption and storage, or even catalysis. However, their use either as catalysts or catalytic supports is limited by their usually low thermal stability. Therefore, another way to take advantage of the excellent properties of MOFs is to use them as sacrificial templates in order to obtain the corresponding metal oxides which preserve to a large extent the properties of the initial MOF.

Two representatives from the aluminium-based MOF series were selected as starting materials to obtain MOF(Al)-derived Ni catalysts: (a) MIL-53(Al), microporous and flexible MOF, and (b) MIL-100(Al), a mesoporous and rigid structure. Ni nanoparticles were deposited on these MOF(Al) structures and then derived by thermolysis under air at 600°C. The as-prepared MOF(Al)-derived catalysts were characterized by XRD, N₂ physisorption isotherms, TGA, SEM/TEM, and temperature-programmed desorption of H₂ and CO₂ (H₂-TPD, CO₂-TPD). The catalytic performance in the methanation of CO₂ was evaluated by temperature-programmed reaction (50 – 500°C) and stability tests at 350°C. It was found that both MOF(Al)-derived Ni catalysts show enhanced catalytic performance in terms of both CO₂ conversion and CH₄ selectivity as compared to a classical Ni/Al₂O₃ catalyst obtained by use of commercial alumina as catalytic support.

Keywords: MOF(Al)-derived catalysts, Ni, CO₂ methanation

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Pure Ni-based and trimetallic Ni-Co-Fe catalysts for dry reforming of methane: Effect of K promoter and the calcination temperature

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Abstract

In recent years, the development of renewable energy sources and the reduction of greenhouse gas emissions have become increasingly urgent global issues. The conversion of CH₄ and CO₂, the two main components of biogas and the major greenhouse gases into synthesis gas is in the focus of academic and industrial research. One of the possibilities to achieve this goal is to react the CH₄ and CO₂ with each other. This work investigates the effect of the potassium promoter and the calcination temperature on the catalytic activity in the dry reforming of methane reaction and compares the performance of the 1%Ni,Co,Fe-Al₂O₃ trimetallic catalysts with the reference 3%Ni-Al₂O₃. Although higher activity was achieved with the 3%Ni-Al₂O₃, trimetallic catalysts resulted in more favorable CO/H₂ ratio and considerably better coke-resistance. Higher calcination temperature generally led to the increase in coke formation, as well as sintering of the catalysts. Promoting samples with 0.5%K in order to improve the coke formation resistance, reduced the catalytic activity.

Keywords: CO₂ methanation, trimetallic catalyst, nickel alloys

Investigation of photocatalytic performances of graphitic carbon nitride on the alumina support

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Abstract

Textile industries significantly contribute to the generation of wastewater containing various raw materials such as cotton, synthetic fibres, and dyes. Textile dyes are harmful to the environment and human health. Therefore, dye-containing wastewater should be treated to preserve the environment, human health, and natural water resources. Nowadays, conventional wastewater treatment methods can be used in the textile industry. However, those methods have some drawbacks like high cost as well as toxic by-products. Therefore, advanced oxidation processes, like heterogeneous photocatalytic degradation can be used as a more appropriate method for dye removal from wastewater.

The present research is focused on the graphitic carbon nitride as a photocatalyst immobilised on the surface of the alumina ceramic ring for photocatalytic degradation of methylene blue (MB) from an aqueous medium under different radiation sources. A metal-free graphitic carbon nitride was prepared through a simple thermal method using urea as a precursor. Deposition of prepared photocatalysts was performed by dip-coating method. The photocatalyst was characterized by XRD, FTIR, and SEM. The photocatalytic activity under ultraviolet (UV-A), visible (warm light), and simulated solar irradiation was examined. The photocatalytic degradation of MB from an aqueous medium was found to increase with increasing irradiation time for all irradiation sources. Furthermore, the radiation source wavelength spectrum plays a significant role in the photocatalytic degradation rate of MB. The immobilised graphitic carbon nitride on alumina ceramic can be convenient for environmental applications, due to easy separation and reusability with high-efficiency removal of MB dye from an aqueous medium.

Keywords: graphitic carbon nitride, alumina ceramic, photocatalysis, methylene blue

Π -Conjugated PolyHIPE photocatalysts through the organocatalyzed reactions and their applications

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Abstract

Conjugated porous polymers (CPPs) with enhanced π -electron delocalization due to the fully conjugated backbone have emerged as promising materials for energy harvesting, storage, and catalysis. Conjugated polymerized high internal phase emulsions (HIPEs), referred to as " π -conjugated polyHIPEs," are a unique subclass distinguished from other CPPs by additional porosity on the larger length scale (pore sizes between 1–100 μm). The HIPE-templated conjugated polymers are currently synthesized exclusively via transition metal-catalyzed polymerization reactions,^{[1],[2]} resulting in residual transition metals in the macromolecular network that negatively affect their performance in photocatalysis. Therefore, the development of organocatalyzed polymerization chemistries for the preparation of π -conjugated polyHIPEs is desirable.

This work summarizes the development of such organocatalytic polymerization approaches for the preparation of organic polyHIPE semiconductors, which were subsequently used as organo-photocatalysts. In this context, the Knoevenagel and Schiff base condensation reactions^{[3],[4]} were used to prepare poly(arylene-cyano-vinylene), poly(azine)- or poly(imine)-based polyHIPEs, respectively. The photocatalytic activity of the synthesized photocatalysts for the photodegradation of aniline in water or transformation of thioanisole under visible light was demonstrated.

Keywords: organo-photocatalysis, π -conjugated polyHIPEs, porous polymers.

References:

- [1] E. Slováková, M. Ješelnik, E. Žagar, J. Zedník, J. Sedláček, S. Kovačič, *Macromolecules*, **2014**, 47, 4864
- [2] S. Jurjevec, G. Žerjav, A. Pintar, E. Žagar, S. Kovačič, *Catalysis today*, **2021**, 361, 146.
- [3] T. Kotnik, G. Žerjav, A. Pintar, E. Žagar, S. Kovačič, *ACS macro letters*, **2021**, 10, 1248.
- [4] T. Kotnik, G. Žerjav, A. Pintar, E. Žagar, S. Kovačič, *Polymer chemistry*, **2022**, 13, 474.

Preparation of TiO₂-Al₂O₃ double-layered inverse opal photocatalysts by both plasma and thermal ALD (Atomic Layer Deposition) methods

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Abstract

Semiconductor-based photocatalyst nanocomposites have attracted significant attention, owing to their applications in various fields, such as the decomposition of organic pollutants, environmental remediation, and energy conversion. TiO₂ inverse opal (IO) was covered by a thin layer of Al₂O₃ a double-layered structure was synthesized via both thermal and plasma-assisted ALD techniques. A 600 nm polystyrene nanosphere template was synthesized by vertical deposition on a glass substrate. The opal was covered by a 50 nm thick layer of amorphous TiO₂ by ALD at 50 °C. The sample was annealed to remove the polymer template at a higher temperature to produce crystalline TiO₂ IO nanostructure in anatase form. Afterwards, the IO was covered by a 5 nm thick layer of Al₂O₃ by thermal and plasma-assisted mode ALD.

The result showed that TiO₂-Al₂O₃ nanocomposites were successfully produced in both methods, and their morphology, composition, structural, optical, and thermal properties were explored by SEM-EDX, UV-Vis, XRD, Raman, and TG-DTA/MS. Besides, the photocatalytic properties of the nanocomposite were investigated by decomposing the methylene blue dye as an organic pollutant under UV light irradiation.

Key words: Photocatalysis, Inverse opal, Nanocomposite, atomic layer deposition

Promotion of electrochemical reduction of CO₂ over SnO₂ by surface hydroxyls and metal doping

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Abstract

Electrochemical conversion of CO₂ into liquid fuels and value-added chemicals is considered to be one of the most promising ways to combat climate change due to anthropogenic CO₂ emissions.^{1,2} Here, we investigated the mechanism of CO₂ reduction (CO₂RR) to formic acid (HCOOH) on a SnO₂ electrode by a combination of density functional theory and microkinetics simulations. We used an implicit solvent model to model the influence of the electrolyte. A major finding is that hydroxylation of the SnO₂ surface does not only lead to improved CO₂RR activity but also to a higher HCOOH selectivity, in part due to inhibition of the competing hydrogen evolution reaction (HER). Another interesting aspect is that the main reaction pathway is via carboxyl (*COOH), while earlier postulates for formic acid formation in CO₂ electroreduction found *OHCO to be the dominant intermediate for SnO₂. We also explored the influence of metal doping of hydroxylated SnO₂ for this *COOH mechanism. A Brønsted-Evans-Polanyi relation for the CO₂ to COOH* step (i.e., the first protonation step) and COOH* to HCOOH (i.e., the second protonation step) on metal-doped (metal = Ni, Pd, Bi, and Cu) SnO₂ surfaces has been identified. Among these dopants, Bi is preferred for facilitating *COOH formation. The activation barrier of the first protonation step decreased from 1.15 eV to 0.93 eV upon Bi doping. A reaction-diffusion model was used that takes into account the effect of electrochemical potential on the stability of intermediates and associated activation barriers in proton-coupled electron transfer steps as well as diffusion of protons and CO₂ from the bulk electrolyte to the electrode surface. Microkinetics simulations confirm that the activity for CO₂RR to HCOOH improved after Bi doping. Our findings indicate that the catalytic activity and selectivity of SnO₂ electrocatalysts can be improved by metal doping.

Keywords: DFT calculation; A reaction-diffusion model; Metal doping; Microkinetics simulations

References:

- [1] Gao, S.; Lin, Y.; Jiao, X.; Sun, Y. *Nature* 2016, 529, 68–71.
- [2] Asadi, M.; Kim, K.; Liu, C. *Science* 2016, 353, 467–470.

Heterogeneous catalysis with copper(II)-bis-aryliminoisoindoline complexes in borate buffer

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Abstract

Investigation for finding the best electrochemical oxidation catalysts looks tedious because of numerous crossroads. In fact, all the branching trails are veins in a leaf of an artificial tree. There is laminar flow in them: some “noble” cylinders run faster while “others” look like standing. The performance of a handful noble metal-containing water oxidation catalysts is so stupendous, that they are incomparable with their relatives of earth-abundant first-row transition metals.

Our team investigates mainly iron and copper containing complexes in both homogeneous and heterogeneous catalysis. A race is in progress to reveal – and enhance – the redox-innocence of copper(II) centre in particular catalysts by choosing the right ligand environment. The aim of this research is to relocate the centre of the catalytic activity by giving the main role to the ligand to develop a cycle where the metal is just a substrate dealer. If it is possible the toll should be known what it takes to run.

We published an article about copper(II)-bis-aryliminoisoindoline complex recently, and investigations are going on with similar but differently substituted ligand bodies. We figured out that they can be homogeneous and heterogeneous water oxidation catalysts depending on the buffering agent and precursors or standalones – determined by their stability.

I will present six complexes in borate buffer and highlight their benefits and drawbacks.

Keywords: water oxidation, heterogeneous catalysts and precursors, borate buffer, redox-innocent metal centre

Preparation and conversion of sugar-based N-alkyl glucamine surfactants

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Abstract

Sugar-derived surfactants are environmentally friendly, biodegradable, non-toxic compounds. They are widely applied in the cosmetics and cleaning industry, but can also potentially be used in conjunction with polymers for enhanced oil recovery in order to extract residual crude oil that cannot otherwise be extracted from oil fields. Compounds of the glucamine type, which contain a sugar head group attached to an alkyl chain via a secondary amine bond, are cationic in nature at acidic pH and thus highly hydrophilic, but behave as nonionic surfactants in alkaline media. Their variants with a not too long carbon chain have favorable water solubility and a moderate tendency to foam.

The direct synthesis of N-alkyl glucamines with preferred properties can be accomplished by reductive amination of mono- or disaccharides with various alkylamines of 8 to 14 carbon atoms under mild conditions. The reaction first yields an unstable imine-type intermediate, which can be saturated to N-alkyl glucamine by complex metal hydride or catalytic hydrogenation. Another way to stabilize the imine, containing the sugar moiety in the form of a cyclic hemiaminal ether, is a selective N-acetylation reaction to furnish an N-alkyl glucamide derivative. Both the imine and its reduced version allow the preparation of gemini surfactants.

In our research, imines were synthesized from anhydrous D-glucose and C8-C14 alkylamines, respectively, by gentle heating the reactants in MeOH. Hydrogenation of the imines was performed in an H-Cube reactor where the hydrogen gas was obtained from the electrolysis of water. This continuous flow method allows extremely efficient, safe and selective reactions at high pressures and high temperatures. Future work will focus on the preparation of gemini surfactants from N-alkyl glucamines with epoxy resins.

A two-step procedure was also developed for the N-acetylation of the imines to furnish glucamide-type compounds. The reaction involves the acid-catalyzed peracetylation of the imine with acetic anhydride followed by selective O-deacetylation with methanolic potassium hydroxide. In our future research, we intend to replace the homogenous base catalyst with a heterogeneous layered double hydroxide.

Keywords: N-alkyl glucamine, sugar based surfactant, reductive amination, acetylation

Supported catalytically active liquid metal solutions (SCALMS) as novel materials for dynamic single atom catalysis – material development and high temperature applications

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Abstract

The use of single atom catalysis (SAC) approach for heterogeneous catalysts has shown to boost the catalytic performance of a metal over their corresponding bulk metal counterpart. For several high-temperature applications, heterogeneous catalysts suffer from deactivation, mainly induced by sintering and coke deposition (coking). Improving the efficiency and stability of such catalysts is a major challenge. Our Supported Catalytically Active Liquid Metal Solution (SCALMS) systems offer unique benefits in addressing these challenges.

SCALMS consists of a solution of a low melting metal, e.g. Ga and an active metal (e.g. Pd, Pt, Rh etc.) that is dissolved in small amounts. The overall solution is deposited on a porous support. This concept was demonstrated for butane dehydrogenation with a Pd-Ga SCALMS (at 400 – 450 °C) and propane dehydrogenation with both Pt-Ga and Rh-Ga SCALMS (at 450 – 550 °C). Surprisingly, rhodium not reported for dehydrogenation became highly active catalysts when deposited in a gallium matrix onto support. We found that under certain compositions, the active metal is stabilized at the liquid alloy interface indicating the SAC nature of SCALMS. The unique reactivity and catalytic performance of SCALMS is attributed to the presence of its highly active and dynamic single atomic sites. In addition, the highly dynamic nature of the liquid alloy interface prevents classical deactivation pathways, such as coking and sintering. Dehydrogenation of propane proceeded with high selectivity toward propene, while little coke deposition was observed by means of high resolution TG-MS. The largest part of the coke originates from the catalyst support.

Keywords: single atom catalysis, SCALMS, dehydrogenation, coking

Investigation of the catalytic activity of Ca-containing clay minerals in biodiesel and fatty acid glucamide production

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Abstract

Biodiesel is a widely used environmentally friendly fuel. Industrial processes, as well as most laboratory research, use edible vegetable oils and methanol to produce biodiesel, and the reaction is carried out in the presence of a homogeneous basic catalyst.

Fatty acid amides are less sensitive to hydrolysis under alkaline conditions, and they can behave as nonionic surfactants depending on their head group. Moreover, they can be produced from either vegetable oil or biodiesel under simple conditions.

During the research work, Ca-containing clay minerals were used as catalysts for the production of biodiesel from vegetable oil by transesterification (or esterification of pure fatty acids with methanol) and the synthesis of alkyl glucamide-type surfactants from edible vegetable oils.

In the first step, we synthesized methyl oleate and coconut oil biodiesel from oleic acid and coconut oil with methanol in the presence of different Ca-containing layered double hydroxides (LDH).

Next, the reaction of methyl oleate and N-methyl glucamine to alkyl glucamide type surfactant was investigated. In this reaction type we tested different solvents and various catalysts (CaCr-LDH, tricalcium aluminate (TCA), $\text{Ca}(\text{OH})_2$, KOH).

The preparation of alkyl glucamide from coconut oil was also attempted with several Ca-containing catalysts.

Finally, we have carried out successful experiments using a flow chemistry method to produce both oleic acid glucamide and coconut oil glucamide with a heterogeneous catalyst.

Keywords: biodiesel, fatty acid amides, clay mineral catalysts

Synergy effect of Cl and Pt on the Brønsted acidity of γ -Al₂O₃ supported platinum catalysts

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Abstract

Introduction

Platinum (Pt) catalysts supported on chlorinated γ -Al₂O₃, consisting of highly dispersed sub-nanometric particles, are widely used in heterogeneous catalysis for numerous applications. While most of studies focus on the reduced state of the catalyst, only few works have dealt with the impact of chlorine on the Pt-oxidized form involved after the catalyst calcination. An improved molecular scale understanding of the chemical interplay between Pt-oxidized and Cl species on the γ -Al₂O₃ surface before reduction is of great interest as these parameters may dictate the properties of the final catalyst.

In that context, the present work reveals the influence of the Cl and Pt on the Brønsted acidity of the calcined catalyst by infra-red (IR) spectroscopy.

Materials and Methods

A coherent series of alumina possessing a wide range of chloration (0, 0.5, 1.0 and 1.4% Cl) and Pt loading (0.3, 0.6 and 1% Pt) where activated under high vacuum (10⁻⁵ mbar) at 723 K after calcination in air. FTIR analysis was performed on self-supported pellets (ca. 10 mg) activated *in situ* using 2,6-di-*tert*-butyl pyridine (2,6-DTBPY) probe molecule.

Results and Discussion

2,6-DTBPY molecule exhibits a high proton affinity (983 kJ/mol) and could be protonated on weak surface acid sites present on chlorinated alumina, contrary to pyridine. The concentration of Brønsted acid sites measured by 2,6-DTBPY increases in a linear fashion with Cl concentration. Moreover, analysis of a coherent series of calcined Pt catalysts supported on γ -Al₂O₃-Cl shows an interplay between the Pt and Cl content, leading to an optimum observed at ca. 1 Cl·nm⁻² in presence of Pt. This result demonstrates the synergy effect between Pt and Cl for the enhancement of the Brønsted acidity of the catalyst. Complementary solid-state NMR and quantum simulations provide further atomic scale insights into the surface hydroxyl groups and the effect of Cl and/or Pt on the chemical properties of the catalyst.

Keywords: Platinum, Chlorinated alumina, Brønsted sites, Infrared, solid state NMR, DFT simulation

CO₂ hydrogenation to value added products over nickel-poor and aluminum-rich layered double hydroxides with different interlayer anions

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Abstract

Carbon dioxide is an abundant carbon feedstock, and there exists a sustainable interest in methods for its utilization. At the moment, a state of the art and fairly simple synthetic path of preparing *NiAl₄-layered double hydroxides (LDHs)* was developed through high-energy mixer milling pretreatment of *Al(OH)₃* followed by impregnation with *Ni(II)* ions from moderately concentrated aqueous *Ni-salt* solutions with various counter ions (*NO₃⁻*, *PO₄³⁻⁻*, *HPO₄²⁻*, *H₂PO₄³⁻*) under mild circumstances (atmospheric pressure and 90 °C). The method proved to be appropriate to build in a large variety of interlayer anions into slightly strange Ni-poor and Al-rich family of LDHs and (*NO₃⁻*, *PO₄³⁻⁻*, *HPO₄²⁻*, *H₂PO₄³⁻*) ions comprising versions were prepared for the first time. Thermally modified LDHs proved to be active in CO₂ hydrogenation reaction at atmospheric pressure. The analysis of data demonstrated that the highest CO₂ conversion was occurred on 550°C temperature for *NiAl₄-LDHs* with different compounds (*NO₃⁻*, *PO₄³⁻⁻*, *HPO₄²⁻*, *H₂PO₄³⁻*), the most contribution of CH₄ selectivity (100%) was occurred on 200-300°C.

Keywords: nickel-poor layered double hydroxides, mechanochemistry, intercalation, CO₂ hydrogenation.

Solution-combustion synthesis of β - $\text{Cu}_2\text{V}_2\text{O}_7$ nanoparticles using two different fuels “Urea and Glycine”: photocatalytic degradation of crystal violet under UV illumination

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Abstract

β - $\text{Cu}_2\text{V}_2\text{O}_7$ nanoparticles were prepared using a solution-combustion method using two different fuels Urea and Glycine. The as-prepared catalysts were characterized using X-ray diffraction, Fourier transform infrared spectra, scanning electron microscopy and UV–vis diffusive reflectance spectroscopy. The photocatalytic activity of copper vanadate was compared by degradation of cationic dye crystal violet in aqueous solution under UV-light irradiation. The effect of catalyst mass, dye concentration and pH solution were investigated using β - $\text{Cu}_2\text{V}_2\text{O}_7$. On the other hand, the reuse tests of β - $\text{Cu}_2\text{V}_2\text{O}_7$ displayed high-performance stability after five cycles.

Keywords: β - $\text{Cu}_2\text{V}_2\text{O}_7$; Solution combustion synthesis; Urea ; Glycine; Photocatalysis

Recent results with a novel electrochemical antioxidant measuring method

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Abstract

Problem

Conventional working electrodes of an electrochemical cell often undergo fouling after a few voltammetric measurements. This can be avoided by modifying the electrode with a thin electrocatalytic layer immobilized on its measuring surface. The redox mediator holding chemically modified electrode allowed introduction of a novel antioxidant measuring method. In order to enhance the applicability of this method several problems needed to be solved.

Method

The method we proposed recently is well applicable for measuring antioxidant activity in different samples. It uses redox mediator modified electrode and chronopotentiometric detection. It does not need application of chemical reagent. The working electrode is a glassy carbon electrode (GCE) modified with Meldola Blue (MB)+(N,N dimethyl-7-amino-1,2-benzophenoxazinium ion) mediator layer. During the measurements, a short controlled potential step is employed to bring the film to its oxidized state. Upon exposing the electrode to reducing samples, the redox potential changes. The initial slope of the electrode potential – time function is used for assessing the antioxidant activity[1]. The initial slope dE/dt is utilized as the signal that depends on the concentration of antioxidant species.

Results

Lately using reduced graphene oxide linker for immobilization of the electrocatalytic film, the sensitivity and stability of the Meldola Blue (MB) layer was improved and the applicability of the electrode for measuring different antioxidant molecules was tested.

Keywords: Chronopotentiometry, Meldola blue, glassy carbon electrode, redox mediator

References:

[1] L. K. Muthuri, L. Nagy, and G. Nagy, ‘Chronopotentiometric method for assessing antioxidant activity: A reagentless measuring technique’, *Electrochem. Commun.*, vol. 122, p. 106907, Jan. 2021, doi: 10.1016/j.elecom.2020.106907.

Mn/Co containing perovskite catalyzed synthesis of pyrimidine compounds

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Abstract

The development of novel catalytic reactions in which readily available alcohols are converted into value-added fine chemicals is a hot topic in the field of synthetic organic chemistry. To build complex organic chemicals around simple or crude raw materials in a tuneable manner, the application of the multicomponent reactions is unavoidable. These enable the syntheses of large libraries of diversely functionalized products in a combinatorial manner. However, for the effective and economical realization of these strategies, high performance catalytic reaction cycles have to be developed.

Nowadays, in the field of multicomponent reactions involving redox cycles numerous studies focused on the development of manganese and cobalt-based catalysts, providing more useful and eco-friendly features compared to commercial ones.

For those reasons, we aim to shine light on the structure–activity relationship in multicomponent pyrimidine synthetic procedure from primary and secondary alcohols and amidines with well-defined and well-characterized MnLaO₃ and CoLaO₃ perovskite catalysts. We are able to demonstrate that simple perovskite oxides are efficient and recyclable heterogeneous catalysts for promoting pyrimidine synthesis selectively. We also show that the alteration in the composition of the catalysts can result in significant differences in their catalytic ability, which effect can be related to the variations in the Lewis acidity of the oxides.

Keywords: alcohol, perovskite, multicomponent reaction, pyrimidine

Insights into the role of Fe-based active phases in CO₂ hydrogenation over Na-Fe₃O₄-Fe₅C₂

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Abstract

Climate change, global warming, fossil fuel depletion and rising fuel prices have created great incentives to seek alternative fuel production technologies. CO₂ hydrogenation to value-added hydrocarbons has been proven to be an emerging solution to fulfill this goal. It has been confirmed that, the combination of Fe-based catalysts and zeolites in the hydrogenation of CO₂ leads to a large degree of product selectivity towards C₅₊ hydrocarbons. However, a great deal of mechanistic understanding regarding the role of active phase formed during the reaction has been yet remained unclear due to the presence of multiple phases of Fe species. In this work, pure Fe₅C₂, and Na and K-promoted Fe₅C₂ are prepared and used to study the relationship between the Fe phases and catalytic performance. First, we adjust the ratio of Fe₃O₄ and Fe₅C₂ to gain insight into the impact of these two active phases in CO₂ hydrogenation. Results reveal that, combination of pure Fe₅C₂ and Na-Fe₃O₄ can increase the CO₂ conversion and the yield of C₅₊ hydrocarbons. However, due to the increased carbon adsorption, CH₄ selectivity also increases. Moreover, carbide addition to iron oxide requires shorter reduction in H₂ before reaction. Furthermore, promotion of Fe₅C₂ with alkali metals could reduce CH₄ while increasing the C₂-C₄ olefin/paraffin ratio, which would be beneficial for further light olefins transformation to C₅₊ in the presence of ZSM-5. This study provides insights in direct CO₂ hydrogenation over Na-Fe₃O₄-Fe₅C₂ catalysts to C₅₊ hydrocarbons, which advances the understanding of the role of active phases of iron-based catalysts in the CO₂ hydrogenation.

Keywords: CO₂ hydrogenation, Fe-based catalysts, active phase, Na-Fe₃O₄-Fe₅C₂

DFT insights into the DDO mechanism of Isoeugenol Catalytic Hydrodeoxygenation on Platinum Cluster

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Abstract

In a scenario of declining fossil fuel reserves and increasing demand for renewable and sustainable alternatives, biomass offers a great potential to complement the depleting energy sources and significantly decrease anthropogenic greenhouse gas emissions into the atmosphere.

Biomass is the only alternative capable of providing carbon based sustainable fuel which can be used directly as a replacement to petroleum. Its conversion to liquid fuels has oriented our study towards catalytic hydrodeoxygenation (HDO), which is currently considered one of the most challenging routes for the upgrading of biomass-derived bio-oils. For this purpose, isoeugenol was chosen as a model monomeric compound of bio-oils, and platinum as reference catalyst for hydrogenation reactions. Clarification of the HDO process of isoeugenol on subnanometer platinum cluster, by means of an atomistic approach based on density functional theory, is the aim of this computational investigation that can be considered as the starting point to investigate possible different reaction paths on different metal clusters, in order to provide experimental chemists with useful tools for large-scale process optimization in the future. HDO was investigated following a direct deoxygenation (DDO) type mechanism which involves the saturation of the allyl double bond, the removal of the methoxy group, the removal of the hydroxy group, and finally the saturation of the benzene ring. DFT calculations identified the formation of the 4-propylphenol intermediate as the rate-determining step and as the pivotal point for one of the most important branching step leading to propylcyclohexanol as a secondary product, for which preliminary results are also presented.

Keywords: DFT, HDO, isoeugenol, platinum, biomass

Chemically programmed synthesis of ZIF-8 and gold nanoparticles with clock reaction

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Abstract

In the past years much effort has been devoted to using chemical clock-type reactions in material design and driving the self-assembly of various building-blocks. A clock reaction (or chemical clock) is a type of chemical reaction in which the product appears suddenly with a well-defined time lag after starting the reaction. Clock reaction is a two-step process with the time scale separation of the reactions. Chemical reactions with different kinetic and mechanistic features can also have an induction period, e.g., autocatalytic reactions, consecutive reactions and enzymatic reactions.

The main motivations for the measurements and research: usage of a clock reaction can be found in the literature, but slightly modified to produce new material structures by self-assembly. We chose the methylene-glycole-sulfite autocatalytic clock reaction connected to ZIF-8 metal-organic framework self-assembly system and gold nanoparticle aggregation system.

The stock solutions of the components in high purity distilled water are injected in a transparent continuously stirred reactor (CSTR), the initial pH is adjusted, and then the reaction is started by adding the catalyst solution. The pH is monitored using a platinum glass electrode and turbidity change of the solution followed spectrophotometrically over time at a giving wavelength. The solid precipitated from the reaction is extracted with filtering or centrifugation, then washed several times and scanning electron microscope (SEM) micrographs will be taken to reveal the crystal structure.

As our research progress, pH-sensitive building blocks (e.g. gold nanoparticles, components of metal-organic frameworks (MOFs)) will self-assembly, even to form new nanostructures in a time-increasing environment, without human invention.

Keywords: clock reaction, MOF, ZIF-8, gold nanoparticles, material design, time-programmed reactions

Synthesis and characterization of heterogeneous catalyst suitable for plastic degradation

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Abstract

This research work investigates the synthesis and characterization of a heterogeneous acidified clay-based catalyst suitable for plastic degradation. Clay obtained from the field was beneficiated by screening to a 150 m mesh size. It was then calcined at 450 °C and acidified with sulphuric acid concentrations of 10%, 25%, 40%, 55%, and 70%. The performance of the synthesized clay was then carried out on shredded polyethylene of a mass of 2 g. The FTIR results of the analysis of the acidified clay catalyst show the presence of carboxyl groups with a wavenumber of 1759 cm⁻¹, indicating degradation of the polyethylene. From SEM analysis, the creation of holes at the interface leads to degradation. The quantitative analysis of the degradation of the polyethylene was achieved by measuring the weight loss of the system from the result. The weight loss was close to negligible, though at higher concentrations the degradation is faster. It is deduced that degradation occurred but at a slower rate.

Keywords: degradation, characterization, catalyst, polyethylene, synthesis, SEM, FTIR

Preparation of porous silica nanoparticles from natural minerals and its application in the catalytic synthesis of carbon nanotubes

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Abstract

In developed countries, nanoparticles derived from natural minerals and high purity chemicals are widely studied. In developing countries like Mongolia, the natural minerals-based nanoparticles have more interest due to the low cost and simplicity of the synthesis route. For the synthesis of natural mineral-based nanomaterials, it is critical first to define the chemical composition and physical structure of local minerals. In order to increase the surface area of the substrate of the nanoparticles, we prepared high surface area porous silica from the clay minerals. We employed an environmentally friendly acid leaching procedure to recover silica from the clay mineral at 25-90°C for 4-48 hours. We applied an organic surfactant (CTAB) with varying molar ratios of Si/CTAB and a simple coprecipitation approach to form nanoparticles on the iron-doped silica nanoparticles. Consequently, we used iron-doped mesoporous silica nanoparticles as a substrate and catalyst for synthesizing carbon nanotubes at 750 °C for 0.5-2 hours in an argon and acetylene gas atmosphere. The physicochemical properties of porous silica substrate and porous silica-carbon nanotube composite samples were characterized using XRD, TG, SEM, XRF, N₂ adsorption-desorption, particle size analyzer, and FTIR spectrometer. Mineral-derived mesoporous silica possessed a porous structure with a large surface area and improved catalytic efficiency and carbon nanotube yield.

Keywords: Mesoporous silica, CNT, mineral, nanoparticle, catalyst

Effect of Reaction Temperature on the Surface Structure and Phase Composition of MnOx-Na₂WO₄/SiO₂ Catalyst for Oxidative Conversion of Methane

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Abstract

Samples of MnOx-Na₂WO₄/SiO₂ based on a mesoporous silica matrix were synthesized using tetraethoxysilane (TEOS), cetyltrimethylammonium bromide (CTAB) as precursors, characterized by scanning electron microscopy with energy dispersive elemental analysis (SEM/EDS), X-ray diffractometry (XRD), electron magnetic resonance (EMR), N₂ adsorption-desorption measurements and tested as a catalyst for the reaction of oxidative conversion of methane (OCM). It is shown that the MnNaW/SiO₂ catalyst consists of MnOx, Na₂WO₄, MnWO₄, and SiO₂ phases. It is assumed that at the OCM reaction temperature of 750–850°C, one of these phases, Na₂WO₄, is in the molten state (the melting point of Na₂WO₄ is 696°C), and under the reaction conditions, a liquid-like phase is formed from the products of the interaction of molten sodium tungstate with MnOx, covering the surface of the crystalline SiO₂ modifications are cristobalite and/or tridymite. The EMR and SEM/EDS data indicate a noticeable effect of the reaction conditions on the surface structure and the distribution of catalytically active components in the catalyst structure. Significant changes in the values of the specific surface area and pore volume of the samples with increasing temperature and duration of the reaction were established (the values of the specific surface area and pore volume, respectively, 116.8 m²/g and 0.590 cm³/g - up to and 46.1 m²/g and 0.232 cm³/g after 15 hours of catalyst operation in the OCM reaction at 800 °C). This example shows the features of high-temperature reactions catalyzed by multicomponent systems, the components of which are in different aggregate states under the reaction conditions.

Keywords: MnOx-Na₂WO₄/SiO₂, surface structure, phase composition, SEM/EDS, XRD

Synthesis and characterization of Co, Pt, PtCo alloy nanoparticles for catalytic CO₂ reduction

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Abstract

The emitted anthropogenic CO₂ in the atmosphere can be considered as waste as well as a contributor to greenhouse effect. To counter this, we aim to convert CO₂ chemically. One of the most promising catalysts are noble metals, however in light of their scarcity and expensive nature, we search for a method which uses as small as possible amounts of it or we fully exchange it for different metals. In this study, samples of Co, Pt and PtCo alloy (different ratios were used per samples) nanoparticles (interface) were synthesized. The synthesized materials were characterized with TEM, XRD, BET techniques. To examine reaction selectivity and product distribution reactions were run in a continuous flow reactor and products were identified via GC. *Ex situ* XPS were used in order to compare the samples in different states: as synthesized, after pre-treatment and after reaction, also to examine the different oxidation states of Co, Pt. We have noted shifts in the peaks of the different states per sample, from which we concluded different catalytic activity. A neutral catalytic carrier was used for this study, the mesoporous silicon oxide - MFC-17. The goal of this project is to examine the catalytic properties of these nanoparticles, to create the best possible method of synthesis as well to determine which composition has the best properties.

Keywords: heterogeneous catalysis, XPS, ex situ, CO₂ reduction, interface

The effect of support nature on the nitridation of MoO_3 and its catalytic activity for ammonia synthesis

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Abstract

Molybdenum nitrides have been investigated for ammonia synthesis, but due to its low surface area of $10 \text{ m}^2/\text{g}$ its activity remains rather low making this the main constraint. In this work we optimized the dispersion of Mo_2N nanoparticles on CeO_2 , TiO_2 , Al_2O_3 , SiO_2 , and SBA-15 (Fig. 1(a)). SBA-15 was shown to be the most appropriate support not only for dispersion, where we were able to reach few-atoms dispersion level with high loadings (up to 30 wt.%, Fig. 1(b-c)), but also the most stable support for the Mo_2N particles. The activity in ammonia synthesis is proportional to the loading as long as the dispersion remains constant and is higher than the unsupported Mo_2N by a factor of 6 for $10\text{MoN}_x/\text{SBA}$. All catalysts were characterized pre and post reaction by XRD, N_2 physisorption, TEM, XPS and XRF.

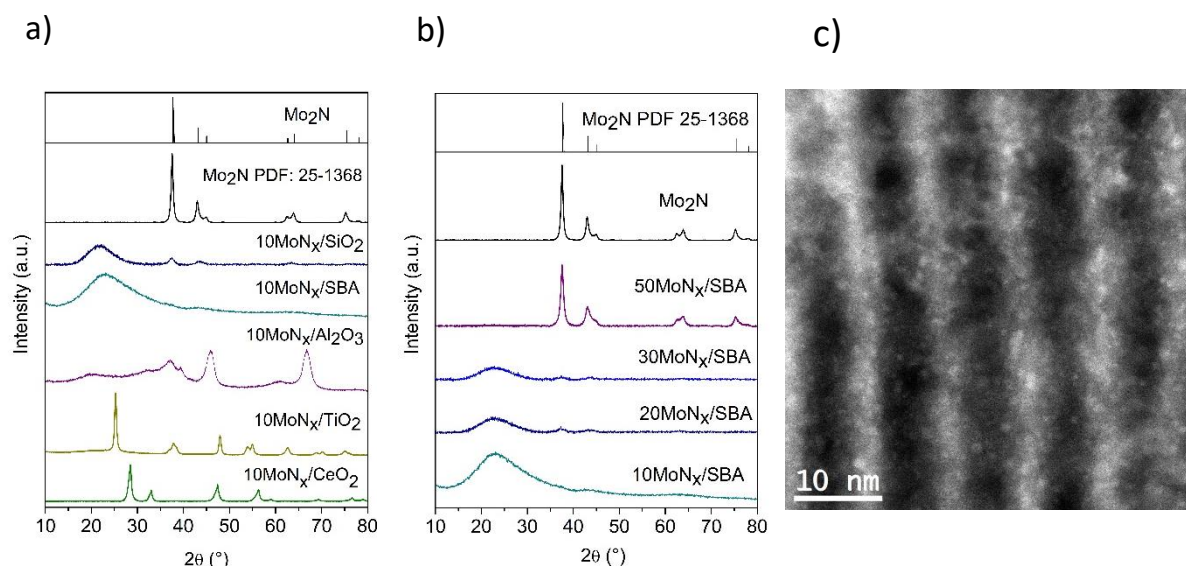


Figure 1. Properties of supported MoN_x catalysts in ammonia synthesis. (a) XRD patterns of MoN_x over different supports ; (b) 10-50 wt.% MoN_x over SBA-15 silica ; (c) HRTEM for $10\text{MoN}_x/\text{SBA15}$

Keywords: Molybdenum, ammonia, supported catalyst

Numerical optimization of catalyst layers in proton exchange membrane fuel cells

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Abstract

Design of proton exchange membrane fuel cell (PEMFC) catalyst layers is a delicate balancing of various transport media (platinum catalyst, conductive carbon, nafion, and porosity). Since platinum is a rare metal, design of catalyst layers is equally important from the view points of both cost and performance.

Determination of optimal composition of the catalyst layers by experiments would be a time-consuming and expensive procedure as there are multiple of design variables. Numerical optimization can be employed to solve such multi-variable design problems. A mathematical model capturing the detailed transport phenomena at catalyst layer is required in this regard. However, such detailed models consist of many highly coupled nonlinear partial differential equations (accounting for conservation of mass, momentum, species and charge) and their simulation usually result in high computational expense. This limits their application for numerical optimization studies. To reduce the computational requirements of detailed models while preserving the geometrical resolution and essential physics, Ly et al. (J. Electrochem. Soc., 156, B1156, 2009) carried out scaling analysis of the model equations and developed an asymptotically reduced model for a single cell PEMFC. Such a reduced model could be suitable for numerical optimization studies on a single cell as well as on stack or system level. In this work, we integrate Ly's reduced model with a non-gradient based optimization algorithm in order to achieve optimal composition of PEMFC electrodes. A multi-objective optimization problem is considered with total catalyst loading and current density (at a given voltage) as two objectives representing capital cost and performance of the cell/electrodes, respectively. The results of multi-objective optimization are then presented in objective space as well as design variable space. A pareto-plot is obtained which quantifies the trade-off between the cost and performance of catalyst layers. The work provides a range of choices to a fuel cell designer where the catalyst loading can be minimized without sacrificing the performance.

Keywords: fuel cells, catalyst layer, optimization, mathematical modeling

Effect of reductive treatment of $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ – carbon composite supported Pt electrocatalysts for PEM fuel cell applications

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Abstract

Composites of titania-based mixed oxides and carbon have recently been identified as promising supports for Pt electrocatalysts in PEM fuel cells. These multifunctional supports bring together the high surface area and electrical conductivity of the carbon backbone with the nanoparticle-stabilizing ability of TiO_2 and the co-catalytic function of the transition metal dopant, which is protected against dissolution by incorporation into the TiO_2 lattice. Since Pt and the oxide component represent a couple liable for material transport effects like strong metal-support interaction (SMSI), a reductive treatment intended to induce such processes may enhance the stability and the performance of the catalyst. The aim of this work is to evaluate the effect of this phenomenon on the structural and catalytic properties of tin-doped TiO_2 – carbon composite supported Pt catalysts.

A 20 wt.% Pt/75 wt.% $\text{Ti}_{0.8}\text{Sn}_{0.2}\text{O}_2$ -25 wt.% C (C= Black Pearls 2000) catalyst was prepared and characterized by XRD, TEM and XPS. XPS measurements combined with H_2 exposure suggested (i) good oxide coverage on the carbon and atomic closeness of Sn to Pt in the initial state of the catalyst, and (ii) formation of a Sn-Pt alloy after a reductive treatment above 200°C. Segregation and oxidation of tin was observed after oxygen exposure of the alloyed catalyst. The electrocatalytic properties and the stability of the parent and the reduced catalysts were compared by cyclic voltammetry and CO_{ads} stripping voltammetry in order to evaluate the effect of alloying and encapsulation of Pt by tin oxide on the performance of the systems.

Keywords: $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$ - carbon composite, Sn-Pt alloying, XPS, electrocatalysis

Acknowledgments

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Nickel-poor layered double hydroxides, synthesis and application in methanation of CO₂ and reverse water gas shift reaction

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Abstract

A mechanochemically way was developed to prepare nickel-poor and aluminium-rich layered double hydroxides (NiAl₄-LDHs) with various type of interlayer anions. The nitrate-, chloride- and sulfate-containing members were already known, but the intercalation of the bromide, iodide, perchlorate and sulfamate anions were attempted for the first time. The chemical quality of the interlamellar anions attested serious influence on the physico-chemical properties and thus the heat-induced topotactic transformation of the LDHs. Thus our aim was to investigate the effect of the presence and departure of the interlayer anions on the catalytic activities of the solids as well. Therefore, the catalysts generated from the LDHs were tested in CO₂ hydrogenation without the generally employed preactivation steps, and the catalytic performance of the pristine and precalcined (500 and 1000 °C) LDH precursors were mapped between 200 and 700 °C.

The quality of the interlayer anions could influence the nature of the catalytic interfaces of the as-prepared solids; the nitrate, bromide and iodide anions departure completely, meantime as residual of the chloride and perchlorate interlamellar anions, nickel(II) chloride phase was present in the *in situ* reduced particles next to the nickel(II) oxide and elemental nickel particles. According to the DRFITS analysis, these catalyst followed the CO₂ hydrogenation pathways toward the formation of methane through formate or carboxylate intermediates. The sulfate and sulfamate containing LDHs attested more complex thermal behaviours and the calcined residues contained sulfur atoms. The analysis of their surface showed nickel(II) sulfide and sulfate phases as well, and these particles served with high CO formation rates due to the observed hydrogen assisted CO₂ dissociation reaction route.

Keywords: NiAl₄-layered double hydroxides, mechanochemical treatment, interlayer anions, interface characterization, CO₂ hydrogenation

Base catalysed transesterification of glycerol with dialkyl carbonates using tricalcium aluminate as catalyst

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Abstract

Glycerol and glycerol carbonate are largely produced from biodiesel which commonly involves transesterification of plant oils. Glycerol carbonate and dialkyl carbonates are high value-added products which are environmentally friendly, they have low to none toxicity and they are biodegradable.

Our aim was to synthesize glycerol carbonate from glycerol in a base catalysed transesterification reaction using dialkyl carbonates as solvent/reagent and tricalcium aluminate (TCA) as catalyst. Although glycerol transesterification reactions have a wide range of literature, tricalcium aluminate has not been used as catalyst, despite its structural similarities to CaAl-LDHs (which are commonly used as base catalysts for glycerol transesterification) and its common occurrence in industrial products and wastes.

In our work, we successfully managed to synthesize glycerol carbonate using TCA as catalyst under reflux conditions with an 80%+ yield after 4 hours for dimethyl carbonate and after 1.5 hours in the case of diethyl carbonate, where the glycerol conversion and the selectivity were followed by a gas chromatography – mass spectrometry method. We successfully decreased the needed catalyst amount in both cases. In addition, other materials were probed and compared to our catalyst under the reaction conditions that were optimized. The reusability of the catalyst was also tested in 4 catalytic cycles and the used catalysts' structures were examined using different techniques such as: X-ray diffraction analysis and Fourier-transform infrared spectroscopy.

Keywords: transesterification, tricalcium-aluminate, glycerol, glycerol carbonate, glycidol

Transformation of hydroquinone with various M(III) metal ion containing Mn(II)-based layered double hydroxides (LDHs)

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Abstract

Hydrotalcite is the most well-known family of the layered double hydroxides (abbreviated as LDHs) category of the mineral anionic clays. Divalent and trivalent metal hydroxides make up their layered structure, when divalent metals are replaced by trivalent metals, positively charged layers form, which are neutralized by negatively charged co-ions building into (intercalate) in the interlayer space. Their versatile chemical compositions make them useful in a variety of modern applications, including polymer additives or (photo)catalysts.

One of the most often used techniques in the synthesis of LDHs is co-precipitation. LDHs were attempted to be prepared utilizing this process employing manganese(II) and several M(III) salts in this study. But, at first, the co-precipitation approach was investigated to generate a novel member of the hydrotalcite supergroup, the MnIn-LDHs, with Mn:In molar ratios ranging from 5:2 to 8:2. The influence of air, N₂, or H₂ atmosphere was extensively investigated. The solids' physico-chemical characteristics were studied in depth using XRD, FT-IR, TG, UV-Vis DRS, SEM-EDXS and ICP-MS. The use of a reductive environment was shown to be essential for producing phase-pure products.

Mn₄M(III)-LDHs were made utilizing the same optimal conditions as MnIn-LDHs, but with M(III) = Al, Sc, Cr, Fe, Ga. For the transformation of hydroquinone in acetonitrile medium, the catalytic performance of several Mn(II)-based LDHs was tested under dark and UV-Vis-illuminated conditions using quantitative ¹H-NMR and gas chromatography – mass spectroscopies. Radical trapping studies were used to investigate the photocatalytic mechanism over MnIn-LDHs, which confirmed that photogenerated holes play a key role in the decomposition of hydroquinone and even benzoquinone. The incorporation of Sc(III), Cr(III), and Fe(III) gave catalysts that performed well both with and without illumination; meantime, several metal oxides/semiconductors, as well as the nonmetallic g-C₃N₄, were inactive under these conditions. The Mn₄Cr- and Mn₄In-LDHs were found to have the highest photocatalytic contributions. The Mn₄Al-, Mn₄Fe-, and Mn₄In-LDHs were shown to have the highest selectivity and yield for benzoquinone production when exposed to UV-Vis light.

Keywords: heterogeneous photocatalysis, comparing tests with various Mn-based LDHs

Behaviour of PtCo alloy nanoparticles catalyzing reverse water-gas shift reaction

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Abstract

Atropogenic CO₂ emission is one of today's most researched topics. The most practical approach is to convert the CO₂ into other compounds, which could be further converted into reagents for the industry. This approach should let us reach carbon neutrality. Since CO₂ is a stable molecule - hence its significant accumulation in the atmosphere - a catalyst should be applied to break its bonds. To achieve this Pt, Co and, PtCo nanoparticles with different Pt:Co ratios (75:25, 50:50, 35:65) were synthesized with similar size and geometry. The metal content and ratios were confirmed with ICP-MS. These particles were loaded onto an inert mesoporous silica, MCF-17. The catalyst materials were characterized via XRD, TEM and BET. Catalytic activity for reverse water-gas shift reaction was tested in a continuous flow reactor, where the products were separated and detected by a GC. The difference in the catalytic behaviour was further elucidated with *in situ* DRIFTS, XPS and UPS measurements. *In situ* DRIFTS allowed us to comprehend the mechanism of the ongoing reaction by identifying the intermediates in the gas phase and adsorbed to the surface of the catalyst. XPS and UPS of the nanoparticles also provided valuable information about the composition of the nanoparticles and how the different alloys are structured, as the peak binding energies of the Pt show significant shifts depending on the coordination with Co in the crystal lattice.

Keywords: heterogeneous catalysis, CO₂ hydrogenation, nanoparticles, PtCo alloy

The behavior of clean metallic nanoparticles in catalytic reactions on boron nitride supports

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Abstract

Nowadays the production of designed catalysts are in the focus of research strategy. For this, the knowledge of the role of the clean components in the catalytic process is unavoidable. It is well-known that the support can greatly influence the catalytic properties of active metal components. In most catalytic technologies, the active metal components are dispersed on high surface area oxide supports. The different dimensionality (0D, 1D, 2D) BN can substitute the oxide support, by which the undesirable oxide-metal interactions can be avoided; moreover, it can allow new beneficial interfacial effects. Concerning the necessity of carbon dioxide removal from the ambient (greenhouse effect, global warming) and the desirable utilization of CO₂ as feedstock, the chemical conversion of CO₂ has attracted increased interest recently.

1D BN nanowire was prepared by precipitation and modified by transition and noble metal. The prepared catalysts were characterized by XRD, TEM, and XPS. It turned out from catalytic studies that the BN nanowires are excellent model support for investigating the pure thermal catalytic behavior of metallic nanoparticles. The metal/BN system performs less activity than the metal/SiO₂ that is usually used as a reference system. The mechanism of the catalytic reaction was established by in situ DRIFTS experiments and the chemical nature of components was monitored by in situ XPS.

Keywords: boron nitride, CO₂ utilization, BN nanowire, model system

Catalytic and inhibiting effects of ash constituents in biomass gasification

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Abstract

In thermochemical processes such as gasification and pyrolysis, the inorganic or ash content of the biomass is a crucial parameter in addition to operating conditions and organic composition, that influence the char reactivity. The inorganic content is present inherently in the biomass or can be externally added by impregnation with aqueous solutions or similar other methods. For gasifiers, the operational issues related to ash are well understood but the role of its constituents on reactivity is complex and needs to be investigated further. The present study investigates the effect of inherent ash constituents and impregnated catalyst on the gasification of char produced from pyrolysis of four leafy biomass (eucalyptus, raintree, mango, jackfruit) and its mixture (garden waste) using a thermogravimetric analyser (TGA) and a fixed bed reactor set-up using CO₂ in the range of 700–950°C. The catalyst (K₂CO₃) was blended with biomass in different proportions to form pellets. The char and CO₂ reactions showed different rates for four garden waste components because of differences in char morphology and inorganic constituents. Eucalyptus char having lower carbon active sites but higher catalytically active (inorganic) sites showed the highest CO₂ adsorption (proportional to reactivity) whereas jackfruit showed the lowest adsorption because of lower catalytic active sites. With similar observations made in the case of mango and raintree chars, the inorganic active sites are inferred to govern the char reactivity to a greater extent than carbon active sites and surface area. The order followed in terms of the char reactivity is eucalyptus > raintree > mango > jackfruit. The trend is also validated against the parameter of alkali index (AI, ratio of basic to acidic oxides) which showed a similar trend. For inherent cases, the catalytic effect is attributed to the inherent potassium species, and the inhibiting effect is attributed to silica and alumina species or their complexes with carbon as identified from FTIR results and findings from a few earlier reported studies. For all the species, char reactivity increased gradually up to 80% conversion with a sharp rise later because of the increase in the ratio of inorganic content to the carbon. The addition of K₂CO₃ as a catalyst enhanced the gasification rate for all biomass species significantly up to 20% loading beyond which the enhancement was marginal. However, the cumulative gas evolution experiments confirmed no change in the product distribution with the addition of catalyst.

Keywords: gasification, inorganic content, char reactivity, alkali index

Fabric Coated with Five Different ZnO Nanoparticles for Efficient Photocatalytic Degradation under Natural Sunlight and UV light

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Abstract

Tuning nanoparticle physicochemical properties for top-notch performance in a colloidal system has been a prime research area in the nanotechnology field. The understanding and development of growth behavior methods and growth kinetics assist a promising tool to modulate the desired characteristics in modeling nanoparticle physicochemical and optical properties. This paper reports the synthesis of five different kinds of ZnO nanoparticles of different morphological, physical, and chemical properties. The supremacy played by the reaction parameters towards the nucleation and growth of ZnO were studied elaborately. Unique morphological structures like rice balls and hydrangea flower petals like structures were obtained with the variation of synthesis medium, methods, and addition of H₂O. Owing to the distinct physical, morphological, and chemical properties, their influence, and interaction with the basic xanthene dye, rhodamine B (RhB) is exhibited uniquely. A remarkably efficient floating photocatalyst was made by treating a fabric with ZnO nanoparticles by facile sonication method, thereby overcoming the hassle and disadvantage of continuous stirring and retrieval of nanoparticles. The 50 ml 10 ppm RhB dye solution was efficiently degraded by ~95% in 100 mins under natural sunlight. The RhB was ~100% degraded under the UV light illumination in 100 mins in the slurry process. Also, the assets and liabilities of the triggering light: natural sunlight, and UV light towards the photocatalyst for dye degradation were studied with illustrated mechanisms. For the first time, this overall study paved the way to find a promising floating photocatalyst that is natural sunlight-responsive.

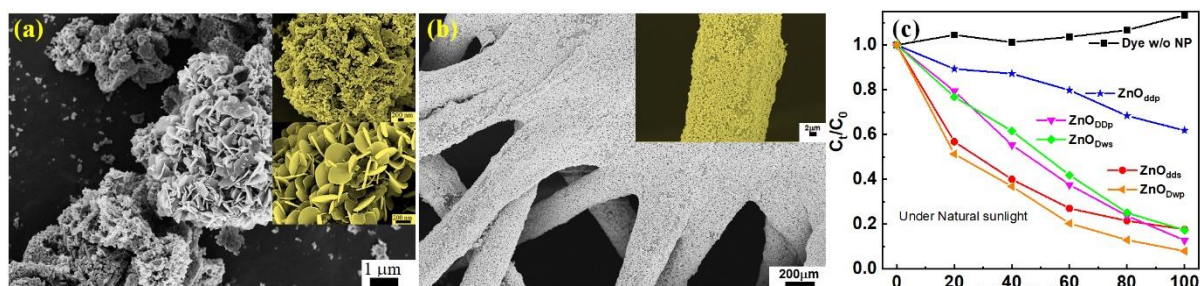


Figure. (a) FESEM images of ZnODws, (b) fabric coated with ZnO, (c) photocatalytic dye degradation under the natural sunlight with five different ZnO

Keywords: nucleation and growth, different morphologies, fabric, rhodamine B, dye degradation, natural and artificial sunlight

Supported CAAC- and BiCAAC-ruthenium complexes on Amberlyst-15

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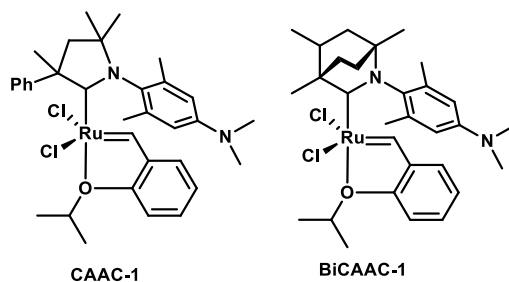
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Abstract

Homogeneous olefin metathesis is a powerful and versatile green method in synthetic organic and polymer chemistry. Although in general, the homogeneous olefin metathesis catalysts render higher activity and functional group tolerance than heterogeneous systems, their separation from the reaction mixture is often cumbersome, thus limiting their industrial application. To combine the advantages of homogeneous and heterogeneous catalysis, there are several examples of the heterogenization of homogeneous catalysts. Since the first solid supported well-defined metathesis catalyst in 1995, numerous reviews summarised this growing area of metathesis chemistry, while their commercial availability are readily growing.

Our group recently synthesized new mono and bicyclic alkyl amino carbene containing ruthenium alkylidenes (**CAAC-1**[1] and **BiCAAC-1**[2]). These complexes showed excellent activity in polar solvents (**CAAC-1**) and at elevated temperatures in the isomerization-metathesis (**ISOMET**) reaction for the decomposition of long-chain olefins to propylene (**BiCAAC-1**). To improve their recoverability and possible recyclability, they were impregnated on different Amberlyst ion exchange resins, since their dimethyl amino group can readily form a strong ionic bond between the complex and the resins sulfonic acid group. The newly impregnated catalysts were analysed and their activities were investigated in model reactions.



Keywords: metathesis, supported catalyst, Amberlyst-15, CAAC

References:

- [1] M. Nagyházi, G. Turczel, Á. Balla, G. Szálas, I. Tóth, G. T. Gál, B. Petra, P. T. Anastas, R. Tuba, *ChemCatChem* **2020**, 12, 1953–1957.
- [2] M. Nagyházi, Á. Lukács, G. Turczel, J. Hancsók, J. Valyon, A. Bényei, S. Kéki, R. Tuba, *Angew. Chemie Int. Ed.* **2022**, DOI 10.1002/anie.202204413.

Visible-light induced photodegradation of amoxicillin catalyzed by NiO-containing titania nanotubes composites with graphene

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Abstract

Amoxicillin is largely utilized for disease control in both humans and animals, causing the contamination of aquatic environment. Its presence in drinking waters raise serious concerns, thereby efficient and green degradation methods need to be developed for their removal. Hence, we prepared a series of composites containing NiO (2.5 wt%), reduced graphene oxide (10 or 20 wt%) or nitrogen-doped graphene (20 wt%) and titania nanotubes for the degradation of amoxicillin as antibiotic model. The surface morphology and structural aspects were assessed by SEM/TEM microscopy, powder X-Ray diffraction measurements and XPS spectroscopy, while the optical characteristics by measuring the DR UV-Vis spectra and calculating the bandgap energies. The photocatalytic performance was evaluated using a visible light LED source and the time evolution of degradation by high-performance liquid chromatography. The influence of graphene (20 vs. 10 wt%) in the composite is clearly shown by a more effective photodegradation of amoxicillin in the presence thermally reduced graphene oxide over the nitrogen-doped graphene. This is due to an improved electron transfer process from titania to undoped graphene, leading to a better charge separation in the photocatalytic process.

Keywords: amoxicillin, photodegradation, Ni, graphene oxide

Sequential Design of Strontium Titanates with Noble Metals (Rh, Ru and Pt) and Nanodiamonds for Enhanced Photocatalytic CO₂ Hydrogenation

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Abstract

The realization of photocatalytic CO₂ reduction on industrial scale remains a matter of concern, which demands a deep investigation for a novel and efficient photocatalyst. Titanate perovskites owing to their excellent photochemical stabilities have shown promising activity towards photocatalytic CO₂ reduction. In the present work, the selective and sequential deposition of noble metals (X= Rh, Ru, and Pt) and nanodiamonds (NDs) were carried out on strontium titanate (STO) photocatalysts i.e., STO-X, STO-X-ND and STO-ND-X. The noble metals and NDs were deposited in either 1 wt% or 10 wt%. The samples were characterized with In-situ as well as ex-situ techniques (XRD, SEM, HRTEM, XPS, DRIFTS, Raman) helped us to understand the structure of the STO and STO-based composites as well as the reaction mechanism under reaction conditions on the molecular level. The results indicated that the sequential deposition of the noble metals and NDs had a positive influence on the photocatalytic activity as well as on the selectivity of the products. The STO-ND-Ru sample had the highest photocatalytic CO₂ hydrogenation efficiency (47.5%) and also showed high selectivity for CO (85.5%) and CH₄ (14.5%). DRIFTS studies showed that the mechanism of the CO₂ hydrogenation followed different routes in the formation of CO and CH₄ with as-optimized STO-ND-Ru and STO-Ru-ND.

Keywords: Strontium titanate, noble metals, nanodiamonds, carbon dioxide, photocatalysis

Optimization of Thermo-Mechanical Properties for Catalytic Ceramic Support Bricks

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Abstract

Catalytic ceramic support bricks warp and spall at high temperatures of application. To enhance thermo-mechanical properties of the catalytic ceramic support bricks the effect of leaching on corundum and particle size were studied. Fresh corundum was analysed using XRD and SEM-EDX. The samples were then leached 3 times for a period of 2½-3 hours at 60-80 °C, respectively. The leachate was sampled at intervals of 30 minutes, cooled to room temperature and pH determined. Leached samples were then dried and analysed using SEM-EDX. SiC nanoparticles were produced using top-down approach. SiC was milled with a planetary mill at 400 rpm for 1hr using Si₃N₄ milling balls. The particles were then pre-treated with a 2M NaCl solution for 1 hour, washed with deionized water, dried in oven and analysed using XRD and dynamic light scattering.

Rietveld refinement simulation quantification of XRD result showed 96.57% α -Al₂O₃, 1.73% NaO.5FeO₂ and 1.52% SiO₂ phase composition of corundum. A plot of pH versus time (minutes) indicated increase of pH from a minimum of 8.19 to 10.43 after 3-hour leaching. The SEM-EDX analysis of leached samples showed appreciable reduction of Na concentration from 2.8 %, 2.0 % and 1.18 % during 1st, 2nd and 3rd leaching respectively. The particle size and shape of the corundum did not change appreciably during leaching. The dynamic light scattering analysis of milled SiC particles showed that the hydrodynamic diameter of milled SiC was on average 502.8 nm.

Keywords: Thermo-Mechanical Stability, Leaching, Milling, SiC nanoparticles, hydrodynamic diameter.

Novel Bacteria-Immobilized Cellulose Acetate/Poly(ethylene oxide) Nanofibrous Membrane for Wastewater Treatment

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Abstract

In this study, electrospun cellulose acetate - poly(ethylene oxide) nanofibrous membrane was found to be unique in immobilizing bacterial cells. Here, removal of methylene blue in aqueous media was achieved by using isolated species of bacteria (*Bacillus paramycoides*) from industrial wastewater and immobilized on cellulose acetate- poly(ethylene oxide) nanofibers using DMSO as a solvent. The decolorization time was varied from 0 to 72 h, different dye concentrations from 20 to 200 mg/L and bacterial cells count was investigated to achieve the maximum MB removal by bacteria-immobilized CA/PEO nanofibrous membrane. The effective dye decolorization was achieved within 48 h and MB removal % was around 93%. Furthermore, reusability of the bacteria-immobilized CA/PEO nanofibrous membrane was tested. It was found that after the 4th usage, 44% of the dye decolorization capacity still could be achieved. These results are promising and suggest that bacteria-immobilized CA/PEO nanofibrous membrane could be economically feasible and eco-friendly when used in MB removal from industrial wastewater. Combination of both adsorption and biodegradation methods was found to be effective in MB removal from aqueous media.

Keywords: Immobilization; Biodegradation; dye removal