Katse

Suomen katalyysiseura
Finska katalyssällskapet
Finnish Catalysis Society

JÄSENKIRJE 1/2017

Arvoisa Katalyysiseuran jäsen!
Dear member of Catalysis Society!

Bioeconomy and catalysis

Bioeconomy is one of the strategic priorities of current Finnish government. In bioeconomy, renewable resources are converted not only to food and feed, but also to chemicals, materials, fuels and energy. For this conversion different technology platforms can be used including bioprocesses, thermochemistry and catalytic conversion. As known, the great advantage of catalytic processes is the good selectivity to desired products and this advantage should also be utilized when converting renewable raw materials especially lignocellulosic biomass to added value products.

However, it has been turned out to be challenging to refine solid biomass to e.g. chemicals and traffic fuels. Processing steps are typically many making the process complex and expensive. Furthermore, impurities in the biomass are very different compared to impurities in crude oil based fractions being main feedstocks for fossil based chemicals and fuels. These challenges set special requirements for the catalysts to be applied for the biomass upgrading and thus special catalysts should be developed for these processes.

In the conversion of lignocellulosic biomass, possible applications of catalysis are many: they can be used together with thermochemical processes such as cleaning and upgrading of gasification product gas or boosting the fast pyrolysis (catalytic fast pyrolysis) or upgrading the pyrolysis bio oil. On the other hand, solid catalysts can be in key role in biorefieries based on biomass fractionation. They can be applied for the hydrolysis of hemicellulose and cellulose as well as dehydration of sugars to furfurals and further upgrading of furfurals to value added chemicals and fuels. Lignin is the most challenging fraction of lignocellulosic biomass, but there has been recent progress in the depolymerization and further hydrodeoxygenation of lignin by heterogeneous metal catalysts. These are only some examples how catalysts can be utilized for biomass upgrading.

As can been seen, catalysis is really in key role in almost all chemical and thermochemical routes from lignocellulosic biomass to chemicals and fuels. However, quite few of these processes have been commercialized so far due to the complexity of these processes. This means that we have to also continue the work to develop more efficient and tolerant special catalysts for the reactions of biomass. This work is going on widely also in Finland and I believe that we'll see new catalyst innovations for more efficient biomass conversion processes in near future.

2nd Finnish Young Scientist Forum for Catalysis

2nd Finnish Young Scientist Forum for Catalysis will be organised 24th March in Jyväskylä. When the event was organised first time in 2016 in Tampere, We had over 40 participants and over 20 presentations mainly by young scientist. We really hope that this will be a new tradition which will gather catalyst researchers annually together. So I hope to see as many of you as possible in Jyväskylä!

Juha Lehtonen
puheenjohtaja
Chairman

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Welcome to the 2nd Young Scientist Forum for Catalysis!

The Young Scientist Forum is here again! This year the symposium will be organized in Nikolainkulma, Jyväskylä on 24th of March, 2017, in connection with the annual meeting of the Finnish Catalysis Society.

In the one-day event, doctoral students and companies are invited to present their research in oral talks, and engage in lively discussion. Contributions from all sub-fields of catalysis are very welcome: homogeneous, heterogeneous, enzymatic and polymer catalysis; presentations covering aspects from theoretical chemistry to material science and chemical engineering.

After the symposium, the annual meeting of Finnish Catalysis Society will take place. All PhD students, their supervisors, and other researchers in the field of catalysis in Finland are cordially welcome!

Set the date in your calendars and visit the web site for further information.

http://web.abo.fi/fak/tkf/tek/youngscientist/

Katalyysiseuran matka-apurahat 2017 / Travel grants of the Finnish Catalysis Society in 2017

Vuonna 2017 Suomen Katalyysiseura jakaa matka-apurahoja nuorille tutkijoille, jotka pitävät esityksen **13th European Congress on Catalysis (EUROPACAT 2017)** –konferenssissa.

Vapaamuotoiset hakemukset toimitetaan osoitteeseen anna.valtanen@oulu.fi 14.4.2017 mennessä. Apurahan saajille ilmoitetaan asiasta henkilökohtaisesti.

In 2017, the young scientists having a presentation in **13th European Congress on Catalysis (EUROPACAT 2017)**–conference are invited to apply for travel grants.

The applications should be sent to anna.valtanen@oulu.fi by 14th of April, 2017. Recipients of grants will be informed personally.

Riikka Puurunen Aalto-yliopiston professoriksi

TkT Riikka Puurunen aloitti helmikuun alussa Aalto-yliopiston kemian tekniikan korkeakoulussa määräaikaisena teknillisen kemian professorina (associate professor) erityisalueenaan katalyysi.

Kuvaaja: Erkki Pöytäniemi

Riikka Puurunen on TKK:n kasvatti. Hän aloitti opintonsa Kemian osastolla vuonna 1994, valmistui DI:ksi neljä ja puoli vuotta myöhemmin ja väitteli tekniikan tohtoriksi vuonna 2002. Jatko-opintoihin sisältyi myös

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vuoden tutkimusjakso K.U. Leuvenissä Belgiassa. Väitöksen jälkeen hän palasi Belgiaan postdoc-tutkijaksi IMEC-tutkimus-keskukseen. Riikka tuli takaisin Suomeen ja Otaniemeen v. 2004 VTT:lle tutkijaksi, josta hän siirtyi Aalto-yliopistoon. Hän jatkaa myös VTT:n osa-aikaisena vanhempana tutkijana tämä vuoden heinäkuun loppuun asti.

Riikka Puurusen tutkimukset ovat fokusoituneet ALD-tekniikkaan ja sen erilaisiin sovellutuksiin. ALD-tekniikkaan hän tutustui jo diplomityössään, joka käsitteli ALD-tekniikan mahdollisuuksia katalyyttien valmistuksessa. Tämä aihealue laajeni väitöstutkimuksissa, jotka käsittelivät itse ALD-prosessia huokoisilla pinnoilla sekä muodostuneiden pintojen karakterisointia. Sen jälkeen Riikan tutkimukset ovat liittyneet ALD:n käyttöön mikroelektroniikan sovellutuksissa ja VTT:llä mikroelektro-mekaanisissä systeemeissä. Varsinaisen tieteellisen tutkimuksen lisäksi hän on tehnyt merkittävän työn kokoamalla erittäin laajasti julkaisuja ALD-tekniikasta eri vuosi-kymmeniltä sekä opinnäytetöitä.

Riikka Puurusella on yli 50 tieteellistä julkaisua ja hänen H-indeksinsä on 20. Hän on toiminut mm. vuosina 2012-2017 Suomen Akatemian rahoittaman Atomikerros-kasvatuksen huippuyksikön VTT:n osuuden projektipäällikkönä. Vuonna 2007 Riikalle myönnettiin Tekniikan Edistämissäätiön Nuoren tutkijan tunnuspalkinto.

Olen iloinnut siitä, että Riikka Puurunen valittiin Aalto-yliopiston professoriksi. Olen tuntenut Riikan hänen opiskeluajastaan lähtien toimiessani hänen opinnäytetöidensä valvojana. Olen oppinut tuntemaan hänet erittäin taitavana, innostuneena ja aikaansaavana tutkijana.

Outi Krause
professori emerita

A new edition of Catalytic Kinetics - Chemistry and Engineering appeared!

A revised and extended edition of the textbook written by Dmitry Yu. Murzin and Tapio Salmi has recently been published. The book provides a comprehensive view on the subject, from the theory of elementary reactions to homogeneous, heterogeneous and enzymatic catalysis. Both the chemical and engineering aspects of the subject are treated very thorougly and numerous examples and exercises are included. The book is printed in paper-back, so the price isvery reasonable.

Dmitry Yu. Murzin & Tapio Salmi: Catalytic Kinetics - Chemistry and and Engineering (ISBN 978-0-444-63753-6), Elsevier, 740 pages.

Catalysis related dissertations in autumn 2016 – spring 2017

M.Sc.(Tech.) Irina Levchuk from the Lappeenranta University of Technology, defended her thesis on 5th of August, 2016. Her thesis entitled *"Titanium dioxide based nanomaterials for photocatalytic water treatment."*.

Opponent: Prof. Pilar Fernandez Ibañez, Plataforma Solar de Almería, Spain

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Custodian: Prof. Mika Sillanpää of Lappeenranta University of Technology

Abstract
Water treatment using photocatalysis has gained extensive attention in recent years. Photocatalysis is promising technology from green chemistry point of view. The most widely studied and used photocatalyst for decomposition of pollutants in water under ultraviolet irradiation is TiO_2 because it is not toxic, relatively cheap and highly active in various reactions.
Within this thesis unmodified and modified TiO_2 materials (powders and thin films) were prepared. Physico-chemical properties of photocatalytic materials were characterized with UV-visible spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectrometry (XPS), inductively coupled plasma optical emission spectroscopy (ICP-OES), ellipsometry, time-of-flight secondary ion mass spectrometry (ToF-SIMS), Raman spectroscopy, goniometry, diffuse reflectance measurements, thermogravimetric analysis (TGA) and nitrogen adsorption/desorption. Photocatalytic activity of prepared samples in aqueous environment was tested using model compounds such as phenol, formic acid and metazachlor. Also purification of real pulp and paper wastewater effluent was studied. Concentration of chosen pollutants was measured with high pressure liquid chromatography (HPLC). Mineralization and oxidation of organic contaminants were monitored with total organic carbon (TOC) and chemical oxygen demand (COD) analysis. Titanium dioxide powders prepared via sol-gel method and doped with dysprosium and praseodymium were photocatalytically active for decomposition of metazachlor. The highest degradation rate of metazachlor was observed when Pr-TiO_2 treated at 450ºC (8h) was used. The photocatalytic LED-based treatment of wastewater effluent from plywood mill using commercially available TiO_2 was demonstrated to be promising post-treatment method (72% of COD and 60% of TOC was decreased after 60 min of irradiation). The TiO_2 coatings prepared by atomic layer deposition technique on aluminium foam were photocatalytically active for degradation of formic and phenol, however suppression of activity was observed. Photocatalytic activity of TiO_2/SiO_2 films doped with gold bipyramid-like nanoparticles was about two times higher than reference, which was not the case when gold nanospheres were used.

M.Sc.(Eng.) Ari Väliheikki from the Faculty of Technology, Environmental and Chemical Engineering, University of Oulu, defended his thesis on 9th of September, 2016. His thesis entitled *"Resistance of catalytic materials towards chemical impurities. The effect of sulphur and biomaterial-based compounds on the performance of DOC and SCR catalysts"*.

Opponent: Magnus Skoglundh, Chalmers University of Technology, Sweden

Custodian: Prof. Riitta Keiski, University of Oulu

Abstract
Exhaust gas emissions, e.g. nitrogen oxides (NO_x), hydrocarbons (HCs) and carbon monoxide (CO), are harmful to human health and the environment. Catalysis is an efficient method to decrease these emissions.

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Unfortunately, the fuels and lubricant oils may contain chemical impurities that are also present in exhaust gases. Thus, catalytic materials with high activity and chemical resistance towards impurities are needed in the abatement of exhaust gas emission.

In this thesis, the aim was to gain new knowledge about the effects of chemical impurities on the behaviour and activity of the catalysts. To find out these effects, the impurities existing in the exhaust gas particulate matter after combustion of biofuels and fossil fuels were analysed. The studied zeolite (ZSM-5), cerium-zirconium mixed oxides (CeZr and ZrCe) and silicon-zirconium oxide (SiZr) based catalysts were also treated with impurities to simulate the poisoning of the catalysts by, e.g. potassium, sodium, phosphorus and sulphur, using gas or liquid phase treatments. Several characterization techniques were applied to find out the effects of impurities on catalysts' properties. The activity of catalysts was tested in laboratory-scale measurements in CO and HC oxidation and NO_x reduction using ammonia (NH_3) and hydrogen (H_2) as reductants.

The results revealed that the CeZr based catalysts had a high activity in NO_x reduction by NH_3 and moderate activity by H_2. Sulphur was proven to enhance the activity of CeZr catalysts in NO_x reduction. This is due to an increase in chemisorbed oxygen after the sulphur treatment on the catalyst surface. Instead, in HC and CO oxidation reactions, sulphur had a negligible impact on the activity of the SiZr based diesel oxidation catalyst. Thus, both CeZr and SiZr based catalysts can be utilized in exhaust gas purification when sulphur is present. ZSM-5 based catalysts were proven to be resistant to potassium and sodium. Alternatively, the activity of SiZr based catalysts decreased due to phosphorus. Thus, the removal of biomaterial-based impurities from the exhaust gases is needed to retain high catalyst activity in the exhaust gas after-treatment system.

M.Sc.(Eng.) Ville Paasikallio from the Aalto University School of Chemical Engineering, defended his thesis on 11th of November, 2016. His thesis entitled *"Bio-oil production via catalytic fast pyrolysis of woody biomass"*.
Opponent: Prof. Wolter Prins, Universiteit Gent (Ghent University), Belgium

Custodian: Prof. Jukka Seppälä, Aalto University School of Chemical Engineering

Abstract
Fast pyrolysis of biomass is a thermochemical conversion process where solid biomass such as wood is thermally converted under a non-oxidative atmosphere at a temperature of approximately 500°C. The main product from this process is bio-oil, a highly oxygenated liquid with very challenging fuel properties. The quality of the bio-oil can be improved using a variety of catalytic processes. One such technology is catalytic fast pyrolysis (CFP), which integrates a catalytic vapor-phase upgrading step directly into a fast pyrolysis process itself. The overall purpose of this is to improve the quality of the bio-oil that is produced in the fast pyrolysis process. This, in turn, can facilitate easier utilization of the bio-oil in demanding applications such as upgrading to transportation fuels. CFP is most often carried out using acidic zeolite catalysts, which are capable of removing oxygen from the pyrolysis vapors in the form of carbon oxides and water. Because both

carbon and hydrogen are lost together with the oxygen, the quality of bio-oil improves at the expense of the yield.

Acidic catalysts and highly oxygenated pyrolysis vapors are a combination which results in rapid catalyst deactivation due to coke formation. In order to maintain an adequate level of catalyst activity, the catalyst must be regenerated on a frequent basis. From the perspective of continuous operation, this sets certain requirements on the reactor technology for CFP. The results of this thesis show that bubbling fluidized bed reactors, which are commonly used for research purposes and do not normally include the possibility of continuous catalyst addition and removal, have clear operational limitations for CFP. Such reactors can, nevertheless, be used for catalyst testing and parametric studies as long as the effect of short-term catalyst deactivation is taken into account.

Circulating fluidized bed reactors with continuous catalyst regeneration provide a much more convenient technological platform for CFP. The effect of coke-induced reversible deactivation is effectively negated, and the focus can be shifted to process performance and catalyst long-term stability. The latter factor is considered to be one of the key questions for CFP. It was shown in this thesis that the combination of biomass-derived inorganic contaminants and severe reaction/regeneration conditions cause irreversible changes in the catalyst structure and properties, which in turn reflects in the quality of the bio-oil. The results of this thesis also highlight the diverse overall character of the CFP products. The partially upgraded bio-oil product is accompanied by a separate aqueous liquid with varying amounts of dissolved organics. Thus, efficient utilization of the CFP products would very likely entail more than one valorization approach.

M.Sc. Bouchra Darif from the Faculty of Technology, Environmental and Chemical Engineering, University of Oulu, defended her thesis on 12th of December, 2016. Her thesis entitled *"Synthesis and characterization of catalysts used for the catalytic oxidation of sulfur-containing volatile organic compounds. Focus on sulfur-induced deactivation"*.

Opponent: Prof. Tapio Salmi, Åbo Akademi, Finland

Custodian: Prof. Riitta Keiski, University of Oulu

Abstract
The work in this thesis concentrates on finding more active and durable catalysts for the demanding environmental application of the oxidation of sulfur-containing volatile organic compounds (S-VOCs). This application is challenging due to the high purification levels required and the catalyst deactivating nature of sulfur. In this thesis, dimethyldisulfide (DMDS) was used as the model molecule to represent S-VOCs since it is often present in odorous emissions and it is more difficult to treat than most of the other S-VOCs.

It was found that the addition of a very small amount of Pt (0.3%) especially improves the selectivity of copper oxide based catalysts towards complete oxidation products ((carbon dioxide (CO_2), water (H_2O) and sulfur dioxide (SO_2)) in DMDS oxidation. Catalyst characterization by transmission electron microscopy, temperature programmed

reduction and X-ray photoelectron spectroscopy analyses suggests that this promoting effect is most likely due to the close interaction between Cu and Pt species on the bimetallic PtCu/γ-Al_2O_3 catalyst.

The drawback of using the Al_2O_3 support is that it is not resistant towards sulfur poisoning. The deactivation of the self-made catalysts was studied with the help of an accelerated ageing procedure that was developed based on the information from the industrially aged volatile organic compound (VOC) catalysts. Industrial deactivation was caused by the sintering of the support and active metals and by the formation of metal sulfates with the support. After accelerated ageing, the silica doped alumina $(Al_2O_3)_{0.8}(SiO_2)_{0.2}$ supported catalyst, showed remarkably promising results in terms of stability towards sulfur poisoning and the activity in DMDS oxidation was very close to that of the most active PtCu/Al_2O_3. The addition of less than 20% of SiO_2 on the Al_2O_3 support led to a catalyst that is more selective and resistant to sulfur poisoning.

M.Sc. Sakari Tuokko from the Faculty of Mathematics and Science, Department of Chemistry, University of Jyväskylä, defended his thesis on 14th of December, 2016. His thesis entitled *"Understanding selective reduction reactions with heterogeneous Pd and Pt: climbing out of the black box".*

Opponent: Prf. Núria López, Institut Català d'Investigació Química, Espanja, and Troels Skrydstrup, Aarhus University

Custodian: Prof. Petri Pihko, University of Jyväskylä

Abstract
Reduction reactions with heterogeneous metals are one of the most important catalytic methods in synthetic organic chemistry. The reduction products are widely used in academic, pharmaceutical, cosmetics, agro-, and fine-chemical industries. A significant challenge for these reactions is to control chemo-, regio-, and stereoselectivity. Although heterogeneously catalyzed reductions are operationally simple, the origins of selectivity are largely unknown, due the lack of understanding of reaction mechanisms on the metal nanoparticles/colloids.

The first chapter of this thesis presents a short introduction to the heterogeneous metal catalysis and a brief discussion about the past and future research of this field. The chapter includes a preview of the fundamental mechanisms and different selectivities obtained with heterogeneous catalysis. The chapter also reviews different experimental and theoretical methods of studying the mechanism of the heterogeneous catalytic reactions.

The second chapter outlines different methods of controlling chemo-, regio-, and stereoselectivity in reduction reactions with heterogeneous transition metal catalysts. The focus of the review is on how the geometry of substrate can affect the reduction reaction in chemo-, regio-, and stereoselective manners. The discussion is divided into two parts: (1) a basic understanding of the factors that affect the substrates' adsorption geometry, and (2) organic modifiers that interact with the substrate by stabilizing transition states and/or reactive conformations. In each case, selective examples are given; however, the main focus is to understand the underlying

reaction mechanisms and origin of the selectivity.

The third chapter consists of research performed by the author towards the understanding of the mechanism of stereo- and chemoselective 1,4-hydrosilylation of enals and enones with heterogeneous palladium catalysts, and further development of the hydrosilylation protocol to a robust and applicable method for industrial use. The chapter also includes studies on selectivity and byproduct formation: (1) first-principle calculations for the mechanism of hydrogenation of acrolein on Pd and Pt, and (2) 3,4-hydroperoxidation of α-substituted enals with heterogeneous palladium catalyst. The research has been performed by the author by combining experimental and theoretical (i.e. DFT) methods. All results are covered more detail in articles I–IV.

Conferences and symposia

ELITECAT 2017 (summer school in catalysis)
July 3-7, 2017, Lyon, France
http://elitecat2017.univ-lyon1.fr/en

13th European Congress on Catalysis (EUROPACAT 2017)
August 27-31, 2017, Florence, Italy
http://www.europacat2017.eu/

8th World Congress on Oxidation Catalysis (WCOC 2017)
September 3-8, 2017, Krakow, Poland
http://8wcoc.icsc.pl/

Forth International Conference CATALYSIS FOR RENEWABLE SOURCES: FUEL, ENERGY, CHEMICALS (CRS-4)
September 4-8, 2017, Adriatic Riviera, Gabicce Mare, Italy
http://conf.nsc.ru/CRS4/

6th International Conference on Semiconductor Photochemistry (SP6)
September, 11-14, 2017, Oldenburg, Germany
http://www.sp6-oldenburg.de/location.html

4th International Congress on Catalysis for Biorefineries, Catbior 2017
December 11-15, Lyon, France
http://catbior2017.univ-lyon1.fr/en

See also e.g.
www.conference-service.com
www.iacs-icc.org/Events/events.html

Web pages

http://www.katalyysiseura.org

http://www.kemianseura.fi

http://www.efcats.org

http://www.elsevier.com

Katalyysiseuran hallitus toivoo, että saisimme jäsenkunnaltamme palautetta Katse-lehdestämme ja uutisia julkaistavaksi (esim. väitökset, kansal-liset ja kansainväliset tapahtumat, palkinnot, kurssit yms.)! Palautteet ja uutiset voi toimittaa hallituksen jäsenille.

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