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GREENCAM for tomorrow

UNIVERSITY OF BUCHAREST
VIRTUTE ET SAPIENTIA

NTNU
Norwegian University of Science and Technology

Materials from biomass

Summer School

September 12th-16th, 2022

NTNU in Trondheim, Norway

Norwegian University of Science and Technology, The main building, Trondheim

NTNU NANO
ENABLING TECHNOLOGY

NTNU
Faculty of Natural Sciences
Department of Chemistry

Welcome to the BioMAT Summer School in Trondheim!

We are pleased to announce that the **BioMat** Summer School now finally is a reality, and we hereby welcome -in special-the «in person attendants», and of course also all the digital attendants. Due to COVID-19 we have postponed the Summer School several times, since it was originally planned to be organised in June 2020.

BioMat is organized by Norwegian University of Science and Technology, NTNU (Trondheim, Norway) in collaboration with University of Bucharest (Romania) in the frame of GREENCAM project. **BioMat** is directed to MSc and PhD students, postdocs and early-career Principal Investigators. Also, professors and researchers from academia and industry with expertise in the field of biomass valorization are invited to participate in the summer school.

The Summer School is dedicated to the research and industrial areas of biomass valorization leading to biofuels and the production of various value-added products. The main aim of this summer school is to offer an overview on the new and innovative aspects from biomass valorization field. Also, the promotion of novel and original strategies related to the production of materials from biomass are considered together with their most important applications at lab as well as industrial scale.

We are very happy to announce that professor Vasile I. Parvulescu (University of Bucharest, Romania) will be presenting his work -in person-at the conference. We are, however, sorry for the inconvenience with the Blue Air trouble, which is the reason that we now also must have digital lectures. However, we are happy to introduce the green online lectures from professor Simona Coman, associate professor Madalina Sandulescu-Tudorache, Dr. Octavian Pavel, Dr. Bogdan Cojocaru and Dr. Delia Popescu, all Department of Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest, Romania.

We are also very thankful and wish to give a special welcome to our local university and industry lecturers: Associate professor Størker Moe (Department of Chemical Engineering, NTNU), MSc. Anna Koziol (NTNU and Crakow University), Dr. Filippo Bisotti (SINTEF), professor Turid Rustad, (Department of Biotechnology, NTNU), CEO Celine Sandberg (Agoprene), Dr. Christian Karl (SINTEF), Dr. Amalie Solberg (RISE-PFI) and Dr. Kristin Syverud (RISE-PFI).

We wish to thank The Education, Scholarship, Apprenticeships and Youth Entrepreneurship Programmer—EEA Grants 2014-2021, Project No. 18-Cop-0041 for financing the GREENCAM project. We are also very thankful to The NTNU Nano IMPACT Fund for financial support and to Department of chemistry, NTNU, for support..

Trondheim September 8, 2022
We hope you will enjoy the Summer School and Trondheim!
Elisabeth E. Jacobsen, NTNU project Manager GREENCAM
Kristoffer G. Paso, Department of chemical Engineering, GREENCAM Team Member
Solon Oikonomopoulos, Department of chemistry, GREENCAM Team Member

Disclaimer: This Summer School is realised with the EEA Financial Mechanism 2014-2021 financial support. Its content (text, photos, videos) does not reflect the official opinion of the Programme Operator, the National Contact Point and the Financial Mechanism Office. Responsibility for the information and views expressed therein lies entirely with the author(s).

GreenCAM

NTNU **NANO**
ENABLING TECHNOLOGY

NTNU
Norwegian University of
Science and Technology

Materials from biomass

Summer School

September 12-16, 2022

NTNU in Trondheim, Norway

Submission deadline for abstracts for student posters: July 31

Send submission to: elisabeth.e.jacobsen@ntnu.no

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GREENCAM for tomorrow

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VIRTUTE ET SAPIENTIA

BioMat Topics:

T1 Materials from agriculture biomass residues
T2 Materials from forest biomass
T3 Materials from food biomass waste
T4 Energy crops
T5 (Bio)chemical system for biomass conversion
T6 Biomass valorization leading to advanced materials

Scientific committee:

Elisabeth Jacobsen, NTNU
Madalina Sandulescu, UniBUC
Kristofer Paso, NTNU
Solon Oikonomopolous, NTNU
Simona Coman, UniBUC

GreenCAM
NTNU NANO ENABLING TECHNOLOGY
NTNU Norwegian University of Science and Technology

Monday September 12, 2022

Zoom link morning session:
https://NTNU.zoom.us/j/94927845106?pwd=aC85VmFBOEMyNVVkdHdaQzIvOW85Zz09
Meeting ID: 949 2784 5106
Passcode: 885703

Zoom link evening session:
https://NTNU.zoom.us/j/95972843003?pwd=YmFaM1RMQmxKME10bk9SKzN4dU0wUT09
Meeting ID: 959 7284 3003
Passcode: 500147

Session chair: Kristofer Paso		
09:00-09:05	Words of welcome **Assoc. Prof Elisabeth Jacobsen, NTNU**	D3-114 Zoom
09:05-09:35	Formation of furans during steam explosion of biomass **Assoc. prof. Størker Moe, NTNU**	D3-114 Zoom
9:35-10:05	Fungal Biocomposites **MSc Anna Koziol, NTNU and Crakow University**	D3-114 Zoom
10:05-10:15	Short break	
10:15-12:00	Steam explosion soft model for softwood chips pre-treatment **Dr. Filippo Bisotti, SINTEF**	D3-114 Zoom
12:00-13:00	Lunch	Element Cantina
13:00-14:00	**Filippo Bisotti, cont.**	D3-114 Zoom
Facilitator: Kristofer Paso		
14:00-14:15	Short Break	
14:15-15:30	Graphenes as multifunctional materials for energy production **Prof. Vasile I. Parvulescu, UniBucharest**	D3-114 Zoom

Tuesday September 13, 2022

Zoom link morning session:
https://NTNU.zoom.us/j/91386109046?pwd=UHd5NVU0V0pVdWVkaTdjM0lDc3NWUT09
Meeting ID: 913 8610 9046
Passcode: 781336

Zoom link evening session:
https://NTNU.zoom.us/j/99906259707?pwd=RERtNzdQc1NkQzlsWGpJaGNjK0IxUT09
Meeting ID: 999 0625 9707
Passcode: 895470

Session chair: Madalina Sandulescu-Tudorache		
09:00-11:00	LAB demonstration for students **Assoc. prof. Solon Oikonompoulos, NTNU**	D2-203
11:00-11:30	Coffee break	Element Cantina
11:30-13:00	Short poster presentations, **posters 1, 2, 3, 5**	R6 Zoom
13:00-14:00	Lunch	Element Cantina
Facilitator: Madalina Sandulescu-Tudorache		
14:00-14.30	Beech wood bio-oil catalytic upgrading at laboratory pilot plant scale: evaluation of the biofuel and carbon deposits **PhD cand. Albert Miro i Rovira**, NTNU	R6 Zoom
14.30-15.10	Chemical recycling of plastic waste **Assoc. prof Kumar Ranjan Rout, NTNU/Quantafuel**	R6 Zoom
15:10-15:30	Tour with demonstration of pyrolysis device by **Albert Miro i Rovira** in the Chemical engineering Hall. All present students	

Wednesday September 14, 2022

Zoom link morning session:
https://NTNU.zoom.us/j/96554064615?pwd=RzN0TkR5ZVAzeWpFVDFXbzVaSTB6Zz09
Meeting ID: 965 5406 4615
Passcode: 791949

Zoom link evening session:
https://NTNU.zoom.us/j/96235435711?pwd=UzZxL1pGeFNXSU1ZaWZuRWxTbHI0QT09
Meeting ID: 962 3543 5711
Passcode: 621483

Session chair: Elisabeth Jacobsen		
09:00-09:45	Biomass valorization based on the enzyme biocatalysis – an important issue for developing a sustainable circular economy **Assoc. prof. Madalina Sandulescu-Tudorache, UniBucharest**	R6 Zoom
09:45-10:00	Short break	
10:00-11:15	Discussion with **Madalina Sandulescu-Tudorache** Group Work	R6 Zoom
11:15-11:30	Coffee break	Element Cantina
11:30-13:00	Chemo-catalytic concepts for biomass conversion to bio-chemicals: a way towards innovative catalytic technologies for a future sustainable economy **Prof. Simona Coman, UniBucharest**	R6 Zoom
13:00-14:00	Lunch	Element Cantina
Facilitator: Elisabeth Jacobsen		
14:00-14:30	Adsorptive materials from waste-a perspective **MSc student Marian-Gabriel, Gâsnac, UniBucharest**	R6 Zoom
14:30-14:50	Poster 5: Biomass valorization by enzymatic grafting of lignin **Dr. Sabina Ion, UniBucharest**	R6 Zoom
14.50-15.10	Biocatalytic method for lignin derivatization with dimethylcarbonate **MSc student Iulia-Maria Constantin, UniBucharest**	R6 Zoom

Thursday September 15, 2022

Zoom link morning session:
https://NTNU.zoom.us/j/97843522083?pwd=SFlJd3lJZ3QzbWhmWHZDSS9ZTEhhZz09
Meeting ID: 978 4352 2083
Passcode: 168148

Zoom link evening session:
https://NTNU.zoom.us/j/99569043644?pwd=eWVvUnJWaVJFY3lKSzZ2WUJCblFXdz09
Meeting ID: 995 6904 3644
Passcode: 398027

Session chair: Bogdan Cojocaru		
09:00-09:45	Biomass and Sustainable Bioeconomy: Dimensions and Challenges **Dr. Delia Popescu, UniBucharest**	R6 Zoom
09:45-10:00	Short break	
10:00-11:00	Discussion with **Delia Popescu** Group Work	R6 Zoom
11:00-11:30	Coffee break	Element Cantina
11:30-13:00	The impact of layered materials with tailored properties in the synthesis of fine chemicals **Dr. Octavian Pavel, UniBucharest**	R6 Zoom
13:00-14:00	Lunch	Element Cantina
Facilitator: Delia Popescu		
14:00-15:00	Hybrid organic-inorganic composites for photocatalytic environment remediation **Dr. Bogdan Cojocaru, UniBucharest**	R6 Zoom

Friday September 16, 2022

Zoom link morning session:
https://NTNU.zoom.us/j/98309714719?pwd=eWdmd043WDRSR0tMQ3FxWUpzTWpEQT09
Meeting ID: 983 0971 4719
Passcode: 251062

Zoom link evening session:
https://NTNU.zoom.us/j/93269859859?pwd=dUhFRDZlNnVTQ0lscmhDT2lMKzk0dz09
Meeting ID: 932 6985 9859
Passcode: 922321

Session chair: Simona Coman		
09:00-09:45	Proteins from marine side streams **Prof. Turid Rustad, Department of Biotechnology, NTNU**	R6 Zoom
09:45-10:00	Short break	
10:00-10:30	Agoprene Alginate Foams - A sustainable alternative to oil-based foams **CEO Celine Sandberg, Agoprene**	R6 Zoom
10:30-13:00	Use of sidestreams to produce biodegradable plastics in a circular economy perspective **Dr. Christian Karl, SINTEF**	R6 Zoom
13:00-14:00	Lunch	Element Cantina
Facilitator: Simona Coman		
14:00-14:30	Alginates - Physiochemical properties and state-of-the-art applications **Dr. Amalie Solberg, RISE-PFI**	R6 Zoom
14:30-15:00	Nanocelluloses in tissue engineering-effects of surface chemistry **Dr. Kristin Syverud, RISE-PFI**	R6 Zoom
15:00-15:05	End of summer School **Prof. Kristofer Paso**	R6 Zoom

Lecture abstracts

Formation of furans during steam explosion of biomass

Størker T. Moe[a,*] Gianluca Marcotullio[b], Mihaela Tanase Opedal[c] and Rune Bruslettto[d]
[a] *Department of Chemical Engineering, NTNU – Norwegian University of Science and Technology, NO-7491 Trondheim, NORWAY*
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Steam explosion is used for deconstruction of biomass. During steam explosion of lignocellulosic biomass, some of the carbohydrates in the biomass are hydrolyzed and subsequently dehydrated to furaldehydes. However, the non-aldehyde furan compound (2-acetylfuran) can also be found in condensates from steam pretreatment of biomass, and established reaction pathways for dehydration of sugars to furans cannot explain the presence of 2-acetylfuran. This work shows how 2-acetylfuran can be formed from known lignocellulosic carbohydrates and suggests plausible reaction pathways.

Potential of fungal biocomposites in thermal insulation applications

Anna Kozioł
annamko@ntnu.no

Nowadays, there has been a rapidly growing interest in providing cheap and sustainable materials. When it comes to construction materials, fungi-based biocomposites turn out to be a promising solution to fulfil growing needs for economical, ecological and environmental materials. Mycelium biocomposites can be grown on a substrate made of low cost waste products (cellulose fibers, reeds or hay). They are biodegradable and, once utilized, can be applied to produce more biocomposites. The downsides are high density compared to currently used polystyrene foams, and high water uptake. However, he ability to modify the end products' properties by adjusting the growth environment creates a way for these materials to be used in set of applications.

Steam explosion soft model for softwood chips pre-treatment

Filippo Bisotti
SINTEF Industry – Process Technology - Kjemisk prosess og miljøteknologi (KPMT Group),
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Steam explosion is one of the most promising biomass pre-treatments prior to saccharification (hydrolysis of complex sugar before fermentation) and pyrolysis (lignin valorisation). The steam explosion aims at disrupting the biomass structure since the lignin fraction which is the most rigid and stiff component of organic matter entangles the inner core constituted of hemicellulose and cellulose. The steam explosion breaks down the lignin cage and allows the release of hemicellulose and cellulose making them accessible to the enzymatic for the conversion into simple sugars (glucose, arabinose, and so forth). The steam explosion step requires strong conditions: the injection of high-temperature and high-pressure steam (190-225°C and 13-25 bar) followed by a sudden depressurization to atmospheric conditions to let the steam expand inside the solid matrix. The steam explosion modelling is quite complex due to several factors: potential lignin condensation due to severe conditions, and further side processes which may lead to undesired by-products. To prevent the lignin from condensation, it is common to impregnate the solid biomass with solvent (acetone, higher alcohols, naphthol and so forth). The workshop will deal with a general soft model to roughly estimate the steam explosion output considering different softwood as biomass-based feedstocks under different operating conditions. The students will solve a system of ordinary differential equations to describe the steam explosion process using Matlab or Excel flowsheet. The analysis will let emerge the impact of the operating conditions and the feedstock composition, as well. The teaching session will include a sequence/iterations of (1) mini-lectures, (2) group discussions, (3) team work, (4) instructor feedback, and (5) individual 5-minute group presentations. Each group will calculate a different type of softwood under different temperature conditions, for example, pinewood, spruce wood, birchwood, etc.

Graphenes as multifunctional materials for energy production

Prof. Vasile I. Parvulescu
Department of Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest, Romania

Since its relative recent discovery graphene attracted a huge interest associated to its multiple potential applications [1]. Initially its synthesis consisted in a simple mechanically exfoliation from graphite [2]. Now it is much diversified. Structural characterization indicated it as an allotrope of carbon consisting of a single layer of atoms arranged in a two-dimensional honeycomb lattice nanostructure. The suffix -ene reflects the fact that this graphite allotrope of carbon contains numerous double bonds. Figure 1,A compiles several properties associated to this structure [2]. Further deposition of metal nano-particles or the functionalization of the surface by different molecules enlarges the properties of these materials [3].

In relation to their high surface area, large electrical conductivity, light weight nature, chemical stability and high mechanical flexibility graphenes have a key role in both energy generation and storage [4]. As an example composites of graphenes with other materials such as perovskites allowed the production of efficient solar panels, while further modification with molybdenum disulphide extends their life-time also for supercapacitors. Other important applications are for advanced heating solutions and smart textiles**.**

In relation to their structural defects, the properties of the graphenes were as well exploited for the synthesis of catalysts and in catalytic applications for selective hydrogenations and coupling reactions (Figure 1, B and C). Combination of these with metal nanoparticles enlarged the class of these reactions.

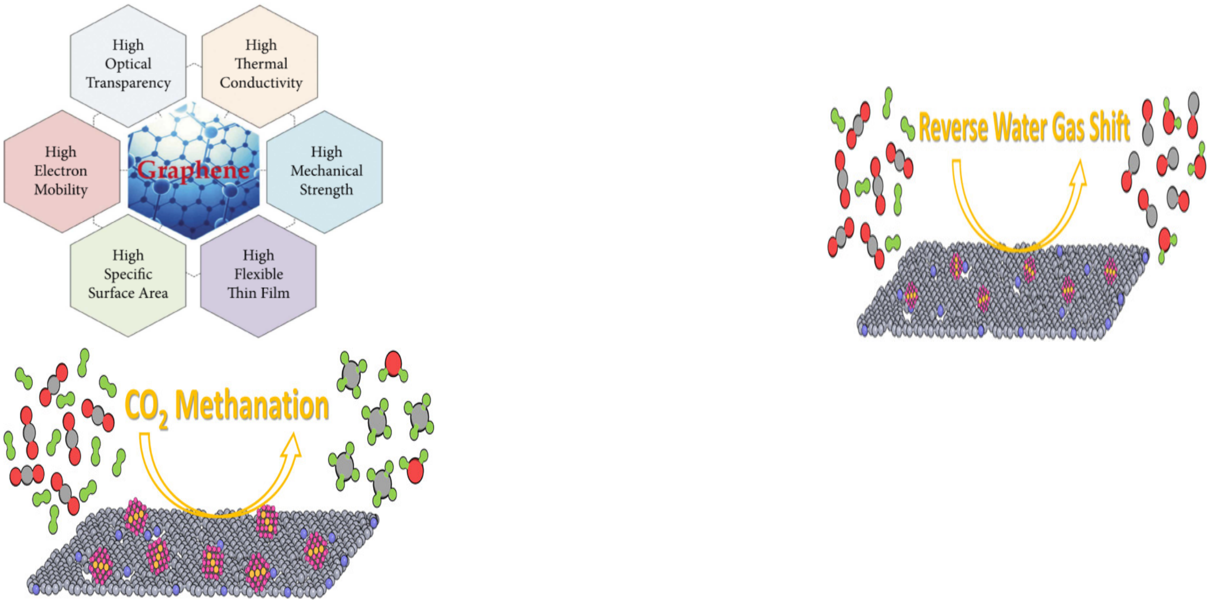

Figure 1. Singles layer structure of graphene and several derived properties (A) and catalytic applications in water gas shift (B) and CO2 methanation (C)

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Adsorptive materials from waste with application in pharmaceutical waste water treatment

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Introduction

The presence of pharmaceutically active compounds (PACs) in the environment and the potential adverse effects they can have is a growing concern for both the public and the scientists. Since they usually are polar molecules, pharmaceutically active compounds are soluble in water. Though the acute toxic effects are unlikely, public awareness was raised after several studies what showed their potential to cause aquatic toxicity. PACs are classified as "contaminants of emerging concern". The main pharmaceuticals' categories found in the waters are antibiotics, pain killers, muscle relaxants and hormonal drugs. Activated carbons possesses good adsorptive capacity due to their large surface area, large porous structure, low cost and preferential affinity for liquid or gas phase. Activated carbons have been proven to be effective for removal of hormones or endocrine disrupting compounds from waters by adsorption[1,2].

Aim and novelty

The project aims to develop new adsorbent materials from waste to purge waste water from pharmaceutical industries. Common technologies used for water remediation, based either on filtrations or on biological treatment (activated sludge) are not suitable for removal of complex polar molecules such are PACs.

Reutilization of the exhausted adsorptive materials

The main disadvantage of activated carbon as an adsorbent is that there is always a need of its disposal after the adsorption treatment.

This project promotes the utilization of waste into multiple useful products generation which may improve waste management and boost the circular economy. The integrated applications of this project describe the commercial window available to accumulate waste materials for large scale applications. Further, sources of energy and nutrients extracted from waste materials after treating polluted water in industries.

Regeneration of activated carbon and other waste materials, after use for treatment of water or wastewater, as low-cost adsorbents are considered a promising, economical process. After adsorption of emerging contaminants, adsorbents lose their adsorption efficacy in aqueous solution bio-chemically due to the presence of acid-oxygen surface groups. To regain the adsorption capacity, pyrolysis of the adsorbents at optimum temperature and holding time regenerated the activation. As well as heat treatment, other treatments such as chemical (using HCl and hot H_2O; liquid phase with H_2O_2 and HNO_3), electro-chemical, physical, and gaseous phase oxidation treatment (with N_2O or O_2) can also efficiently remove surface groups causing reduction of sorption efficiency [3].

Nutrient recovery from wastewater sources is not a new concept, however waste material disposal to barren lands after adsorbing emerging contaminants, especially micropollutants, from wastewater is a new approach to improve soil fertility. This process can be implemented not as a major revenue stream for wastewater treatment but rather as an offset to the water treatment cost and to meet nutrient recovery and environmental goals set by nutrient discharge regulations. For instance, nitrogen and phosphorus are considered as two of the most critical components controlled under for wastewater treatment regulations. Other nutrients such as Mg, Ca, Zn, K also play significant roles for soil and plant growth but the process to produce such elements in fertilizer can be costly. Nutrient adsorption by waste materials can not only be approached for the cost-effectiveness for water treatment, wastewater adsorbents enriched with micro and macro elements can also be the potential carrier for extractable resources as well as to mitigate the environmental hazards due to the eutrophication of industrial effluent [4].

Cementitious materials are used as binding materials for concretes in buildings and construction. Chemically they are complex bonded mixtures of calcium silicates or calcium hydroxides and they react with water to produce hydration products. Cementitious materials are used as binding materials for concretes in buildings and construction. Chemically they are complex bonded mixtures of calcium silicates or calcium hydroxides and they react with water to produce hydration products [5].

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Biocatalytic method for lignin derivatization with dimethylcarbonate

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Introduction

Lignin is a phenolic derivate and it is the second most abundant biomass compound after cellulose. It is a polymer made of 3 alcohols: cumarilic alcohol, coniferilic alcohol and sinapilic alcohol. It is predominantly found in the cell wall of woody plants and together with cellulose are the main constituents of wood.
The structure of lignin is formed by cross-linking the three phenolic precursors, also known as monolignols. [1]
The leading uses of lignin at the moment are: as fuel, as stabilizing agent for aliminium oxide solutions and as part of nanostructures or biological systems. [2] Due to its highly natural composition, lignin is a good biodegradable material. Also, the utilization of more lignin based products would reduce environment pollution. [3]
The latest studies reveal that the process of biomass transformation in active carbons can be used for energy stocking. The natural porosity of lignin is a great advantage regarding this area of research. [4]
Despite its abundance, this resource has few known applications. The production cost is minimal, because it can be collected from numerous vegetal processing industries: paper manufacturing, cellulose manufacturing and many others. [5]

Experimental

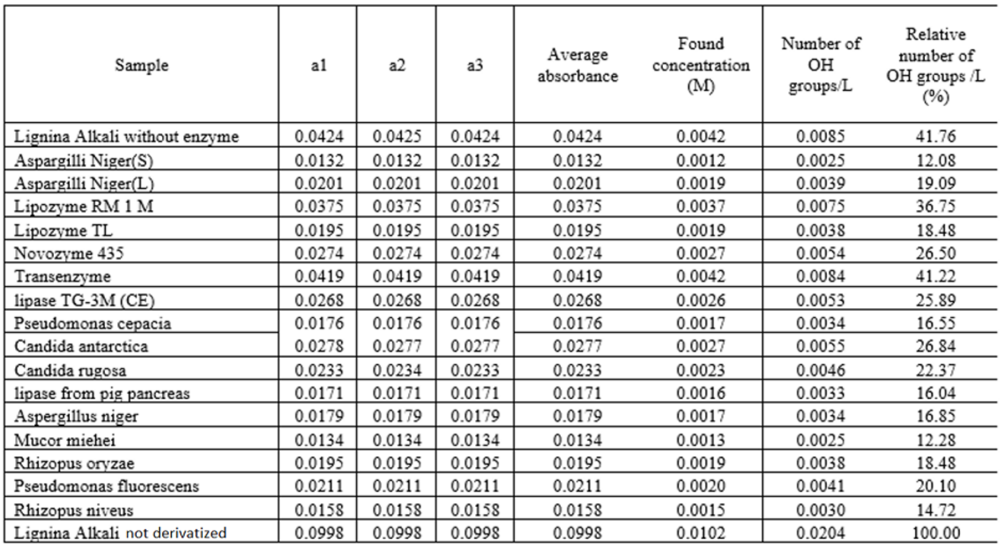
The goal of this experimental study was emphasizing the possibility of lipaze-assisted derivatization of lignin with dimethylcarbonate.
Lignin derivatization is a continuously evolving process which creates new materials with better properties and superior efficiency meant to improve human livelihood and reduce pollution.
The methylation of lignin has applications in the industry of synthetic fabrics. The chemical reaction takes place at the phenolic hydroxyl and the resulting compounds are easier to handle during the industrial processes than the initial polymer. [6]
Many types of biocatalysts were tested in this study in order to find the one with the best yield. The samples consisted in both simple enzymes and imobilized enzymes. After the carboximetylation of lignin, the final compound's structure was analysed by FTIR. The degree of derivatization was determined by Folin-Ciocalteu method.

Results

After the completion of the derivatization process, the samples were analysed using Folin-Ciocalteu method alongside with a sample of lignin that was not altered, in order to compare and analyse the number of OH sites that were changed.

The Folin-Ciocalteu reagent used in the assay is a mixture of phosphomolybdate and phosphotungstate. It is used for the colorimetric in vitro assay of phenolic and polyphenolic antioxidants. This method is based on selective oxidation of phenolic hydroxyls. The oxygen resulting from the reaction will oxidate the molibden from 2+ ion to 4+ ion thus forming the blue coloration. The detection method is UV-Vis spectroscopy, in the current study the wavelength were from the UV spectrum .

Folin-Ciocalteu analysis for derivatized lignin (solid phase)



Sample	a1	a2	a3	Average absorbance	Found concentration (M)	Number of OH groups/L	Relative number of OH groups /L (%)
Lignina Alkali without enzyme	0.0424	0.0425	0.0424	0.0424	0.0042	0.0085	41.76
Aspargilli Niger(S)	0.0132	0.0132	0.0132	0.0132	0.0012	0.0025	12.08
Aspargilli Niger(L)	0.0201	0.0201	0.0201	0.0201	0.0019	0.0039	19.09
Lipozyme RM 1 M	0.0375	0.0375	0.0375	0.0375	0.0037	0.0075	36.75
Lipozyme TL	0.0195	0.0195	0.0195	0.0195	0.0019	0.0038	18.48
Novozyme 435	0.0274	0.0274	0.0274	0.0274	0.0027	0.0054	26.50
Transenzyme	0.0419	0.0419	0.0419	0.0419	0.0042	0.0084	41.22
lipase TG-3M (CE)	0.0268	0.0268	0.0268	0.0268	0.0026	0.0053	25.89
Pseudomonas cepacia	0.0176	0.0176	0.0176	0.0176	0.0017	0.0034	16.55
Candida antarctica	0.0278	0.0277	0.0277	0.0277	0.0027	0.0055	26.84
Candida rugosa	0.0233	0.0234	0.0233	0.0233	0.0023	0.0046	22.37
lipase from pig pancreas	0.0171	0.0171	0.0171	0.0171	0.0016	0.0033	16.04
Aspergillus niger	0.0179	0.0179	0.0179	0.0179	0.0017	0.0034	16.85
Mucor miehei	0.0134	0.0134	0.0134	0.0134	0.0013	0.0025	12.28
Rhizopus oryzae	0.0195	0.0195	0.0195	0.0195	0.0019	0.0038	18.48
Pseudomonas fluorescens	0.0211	0.0211	0.0211	0.0211	0.0020	0.0041	20.10
Rhizopus niveus	0.0158	0.0158	0.0158	0.0158	0.0015	0.0030	14.72
Lignina Alkali not derivatized	0.0998	0.0998	0.0998	0.0998	0.0102	0.0204	100.00

The results showed that all the lipazes did catalyze efficiently the dervatization process, however, the imobilized enzymes did not have such a good yield because of the steric repulsions: given the voluminous stucture of lignin, the fact that the imobilized enzymes have a bulkier frame than the simple ones decrease the catalysation abilities in this case.

The collected and analysed data determined the most efficient enzyme, lipaze from *Aspergillus niger* (S), followed closely by the ones from *Mucor miehei* and *Rhizopus niveus.* All these three are good choices for lignin carboxymethylation.

Conclusions

The future perspectives of this study will include the optimization of the lignin derivatization system with dimethylcarbonate. Futhermore, the processed compounds will have their physical properties analysed in order to establish if they can be used in industrial mechanisms.

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Biomass valorization based on the enzyme biocatalysis – an important issue for developing a sustainable circular economy

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Today, biocatalysis is considered to be one of the most suitable alternatives to chemical catalysis, especially dedicated to biomass valorization (conversion of biomass into value added products). Both biocatalysis and biomass conversion are playing an important role for the development of a sustainable circular economy with the main target of replacing the fossil resources by the renewable raw materials from biomass. [1]

Biocatalysis can be defined as the catalytic biotransformation based often on the enzyme catalyst. As a typical catalyst, the enzyme can only accelerate reactions without impact on the thermodynamic equilibrium of the reaction. High substrate tolerance is exhibited by the enzyme accepting a large variety of nonnatural substances [2]. This aspect had been substantially improved when the catalytic promiscuity of the enzyme has been discovered [3]. So that, unrelated substrates can be bound to the same active site of the enzyme structure. An eloquent example is the lipase enzyme which catalysis naturally the hydrolysis of lipidic compounds or esterification/transesterification reaction of alcohol and fatty acids. In the beginning of '90, lipase started to be used as catalyst for the epoxidation of carbon double bound. Today, the accidental catalytic promiscuity is not significant in the field of biomass valorization. However, there are enough aspects which offer signals that the biocatalysis promiscuity will be relevant in a close future, especially for the production of the value-added compounds in industrial areas. [3]

Typically, the process mediated by an enzyme has faster kinetic (TON >> 10^2) comparing with the classic catalytic alternative. As a consequence, enzyme low concentration (10^{-3} – 10^{-4} % of enzyme) is required for an efficient catalytic process [2]. If we consider also the enzyme immobilization alternative for the construction of a biocatalyst allowing to reuse the biocatalyst preserving the catalytic activity, the myth of high cost of an enzyme biotransformation is destroyed. In this context, it should be mentioned that reasonable price of enzyme is our reality due to advanced molecular biology. [3]

An important advantages of the enzyme biocatalysis is its selectivity divided in three major types: (i) chemoselectivity, (ii) regioselectivity/ diastereoselectivity, and (iii) enantioselectivity. Advanced selectivity offered by an enzyme catalyst placed the enzyme above the conventional catalyst on the scale of the efficiency in catalysis. Beside these, the enzyme exhibits biodegradable properties and catalytic activity under mild conditions (*e.g.* pH 5-8, temperature range of 20-40°C, and room pressure). Consequently, enzyme biocatalysis is a potential strategy for chemical processes with applicability for biomass valorization in the perspective of a sustainable circular economy. [2]

It is well known that the actual industrial applications rely mainly on the fossil resources. However, the fossil sources are limited and their stock cannot be refilled in a short time. In addition, they are expensive and their exploitation has a negative impact on the environment. These are the main arguments taken under consideration to launch the new research strategies using biomass as renewable carbon source. So far, the biomass composition used as feedstock imposed at least three general platforms, such as polysaccharides, terpenes and combustibles. Biocatalysis for polysaccharides lead to fuels and fine chemicals following equally the degradation and modification of the substrate. Also, chemical modification/derivatization strategy based on enzymatic catalysis is often considered for terpenes valorization. In this context, our research group explored the lignocellulose, turpentine, and oil as biomass samples with suitable composition for promising renewable C sources. Lipase-based biocatalysis systems were adapted for biomass valorization leading to added-values products with high impact on food, cosmetics and pharmaceutical areas.

Lipase biocatalysis is a valuable example of enzyme biocatalysis for the industrial area. Lipase enzymes become from the hydrolases family with the effect on the carboxylic ester bonds. Physiologically, lipase catalysed the hydrolyses of triglyceride leading to di-/mono-glycerides, fatty acids and glycerol, but it can assist the (inter/trans)-esterification reactions in nonaqueous media, too. Based on this versatile behaviour, lipases are one of the most useful enzymes in industrial area with many industrial applications developed in the food, detergent, and pharmaceutical industries. Limonen/α-pinene/menthol derivatives, modified lignin, silybin esters, glycerol carbonate and glycidol are few examples of the reaction products based on lipase biocatalysis developed in our lab. The examples will be detailed below in order to demonstrate the high impact of lipase on the efficiency of the process biocatalysis, especially for biomass valorization as renewable raw materials in the context of a sustainable circular economy.

Biocatalytic strategy for lignin derivatization (modification of the chemical structure) is an important target of our research activity [4, 5]. Lignin is a complex heterogeneous 3D bio-polymer with enormous potential to replace fossil-based resources for the sustainable production of many chemicals and materials, including petroleum-based products. It is one of the most abundant natural bio-polymers with strong intra/inter-molecular hydrogen interactions often modified after pulping processes leading to large variation of the lignin properties. For tailing lignin properties such as composition or functional groups, key enzymes can be used leading to new polymers with predictable properties [4]. In our study, we investigated biocatalytic routes for the addition (insertion) of functional groups in the lignin chemical structure. A proposed alternative involves carboxymethylation of lignin (CML) using dimethyl carbonate (DMC) as derivatization reagent and lipase as biocatalysts. The success of the carboximethylation process was demonstrated by ^{13}C-NMR results supporting the lignin carboxymethylation as a mean result, where carbonate carbonyl carbons were detected at 154 ppm. The FTIR spectra collected before and after the carboxymethylation process evidenced as well the lignin modification. Additionally, the CML was characterized using conductivity measurements, gel permeation chromatographic analysis (GPC), thermogravimetric analysis (TGA), temperature-programmed desorption (TPD-NH_3/CO_2), scanning electron microscopy (SEM), and nuclear magnetic resonance (NMR) analyses. All these characterizations provided clearly evidences of the modification of lignin properties as direct effect of the biocatalytic lignin derivatization.

Lipase-based biocatalytic system has been developed for the epoxidation of α-pinene leading to its oxygenated derivatives [6-8]. α-Pinene treated with an oxidation reagent (H_2O_2/ UHP/ TBHP) and carboxylic acid derivative (ethyl acetate) using lipase enzyme as biocatalyst led to the desired epo-oxidation products. Ethyl acetate played double role, *i.e.* acetate-supplier and organic solvent. Different immobilisation approaches were tested for the lipase biocatalyst preparation, *e.g.* CLEA, CLEMPA and covalent immobilization. Biocatalysts performance was evaluated in term of activity, substrate conversion and selectivity of the epoxy products. Additionally, the biocatalyst behaviour was correlated with its textural characteristics. Maximum of 65 % conversion of α-pinene was achieved for CLEMPA biocatalyst design preserving the catalytic activity for several successive reaction cycles (70 % recovery of the catalytic activity after six reaction cycles). [7, 8]

Our research group developed several biocatalytic systems for glycerol (Gly) conversion into glycerol carbonate (GlyC) as an interesting solvent with promising perspective in the area of Green Chemistry [9-15]. Homogeneous and heterogeneous biocatalysis have been performed for GlyC synthesis. Gly was chemically transformed into GlyC using lipase biocatalyst from *Aspergillus niger* source. Homogeneous biocatalysis allowed to convert 74 % Gly with 80 % selectivity of GlyC under mild conditions (DMC used as reagent and reaction medium, 4 h reaction time and 60°C temperature) [9]. Heterogeneous biocatalytic strategy (covalent and CLEMPA design of the biocatalyst) allowed to reach advanced biotransformation of Gly specifically into GlyC (52 and 73 % Gly conversion with 90 and 77 % GlyC selectivity for covalent and CLEMPA biocatalyst, respectively) [10]. Moreover, crude Gly was used successfully for GlyC synthesis (49 and 70 % Gly conversion with 91 and 80 % GlyC selectivity for covalent and CLEMPA biocatalyst, respectively). [11-14]

Recently, cold-active lipase-mediated biocatalytic system has been developed in our research group [15]. The system was dedicated to the silybin acylation with methyl fatty acid esters based on the extracellular protein fractions produced by the psychrophilic bacterial strain *Psychrobacter* SC65A.3 isolated from Scarisoara Ice Cave (Romania). Multiple immobilization approaches of the cold-active lipases (using carbodiimide, aldehyde-hydrazine, or glutaraldehyde coupling) allowed the construction of bio-composites (S1–5) with similar or even higher catalytic activity than free lipase under cold-active conditions (25°C). The immobilization strategies involved covalent attachment of the enzyme to nano-/micro-sized magnetic or polymeric resin beads. Characterization methods (e.g., FTIR DRIFT, SEM, enzyme activity) were used for the evaluation of the prepared bio-composites. Additionally, they exhibited between 80 and 128% recovery of the catalytic activity for protein loading in the range 90–99% [15]. This led to an immobilization yield up to 89%. The biocatalytic acylation performance reached a maximum of 67% silybin conversion with methyl decanoate acylating agent and nano-support immobilized lipase biocatalyst. [15]

Based on the lipase biocatalysis examples detailed abouve, the main conclusion is that the biocatalysis is still promising alternative for transformation of biomass compounds into valuable added products with impact on the industrial life especially by the development of a sustainable cyclic economy which can provide long-term improvement of our society life.

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Chemo-catalytic concepts for biomass conversion to bio-chemicals: a way towards innovative catalytic technologies for a future sustainable economy

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The development of innovative catalytic technologies to transform biomass into chemicals attracts increasing interest in both academic and industrial areas as a means to establish a sustainable economy. In this context, will be presented the most relevant concepts developed in the field of chemo-catalytic conversion of biomass and will be proposed strategies for the design the future generations of catalytic processes devoted to the production of chemicals from lignocellulose-derived compounds. Will be discussed (i) approaches currently followed in the selection of biomass conversion routes to chemicals, (ii) required operating conditions to process bio-derived feedstocks, and (iii) design features for efficient catalysts. With regards to catalyst families, carbon-supported metals and resins seem to offer good perspectives for application to biomass conversion. Zeolite-based catalysts also have a high potential for upgrading in the future bio-based chemical industry, owing to their intrinsic properties and especially in view of their extraordinary versatility. A very preliminary but perceptible step in this direction has been shown based on the performance of tailored (hierarchical and/or functionalized) zeolite-based systems which attain superior performances in the transformation of bio-based compounds. Throughout the way from idea towards industrial reality, will be presented scientific and technological aspects of the mature petrochemical industry that could be transposed or adapted to the bio-based manufacture of chemicals.

Biomass and Sustainable Bioeconomy: Dimensions and Challenges

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Bioeconomy is an important element of sustainable development, becoming increasingly relevant at the national, EU, and global levels. Addressing the numerous societal challenges of the twenty-first century, such as the transition from an economy based on fossil raw materials to a bioeconomy, obtaining raw materials from renewable biological resources, etc., requires intensive concerted efforts from national and international institutions in agreement with industry sector representants, and also promotes the development of policy strategies in the field of bioeconomy. Biodegradability, environmental friendliness, and sustainability are the key features that have made biomass the primary candidate for the development of a sustainable bioeconomy. Biomass is the most promising renewable source at the moment. Sources, availability, production, and chemical composition of biomass will be presented, along with optimal uses, conversion, and sustainability of biomass. Strategies for optimal use of biomass in the bioeconomy will be highlighted. The role of biomass in the bioeconomy is addressed, with an emphasis on the European Union, but significant developments in other regions of the world are included as well. The conversion of biomass into refined products like chemicals, fuels, wood and paper products, heat, electric power, etc. will be reviewed. A socio-ecological perspective will be provided, as well as some challenges and ethical aspects associated with biomass supply, production, and exploitation. In the last part, several international case studies will be discussed to illustrate the importance of biomass and bioeconomy in sustainable development.

The impact of layered materials with tailored properties in the synthesis of fine chemicals

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As part of the anionic as well as 2D materials types, the tailored layered double hydroxides (LDHs) or hydrotalcite-type materials (HTs) continue to exhibit a great interest considering their physicochemical properties which are used in different domains, *i.e.* pharmacy, medicine, catalysis, environment protection, etc. [1]. The so called memory effect has also been mentioned as an important property of these materials [1]. Traditionally, LDH can be synthesized by co-precipitation (low / high supersaturation, urea hydrolysis), ion-exchange, rehydration using structural memory effect, hydrothermal, secondary intercalation, etc. However, these methods show important disadvantages: *i)* uses inorganic alkalis (*i.e.* NaOH, Na_2CO_3, KOH, K_2CO_3, etc.) which most often contaminate the final solid with the constituent alkaline cations, and *ii)* large amounts of energy and water are consumed in their synthesis.

The workshop will deal with the presentation of non-traditional methods for syntheses of different type of LDH using a variety of *mono-*, *di-* and *tri-* valent cations as well as parameters that can be used / modified (*i)* adjusting the operational parameters of procedures, *ii)* changing of the alkali nature uses for the pH control (inorganic *vs.* organic), *iii)* the composition of the cationic and anionic layers, *iv)* the presence / absence of the aging step, *v)* the type of solution used to reconstruct the layered structure, etc.) in order to generate tailored physicochemical properties that improve the catalytic behaviors in the synthesis of various important compounds using several types of reaction (selective oxidation of cyclohexene, cyclooctene, styrene, 5-hydroxymethyl furfural; cyanoethylation; Knoevenagel and Claisen-Schmidt condensation).

Different methods for synthesizing hybrid materials such as curcumin-LDH, as powders or films using the MAPLE procedure, and data on the release of curcumin (CR) will be presented, knowing that it is a powerful biomass-derived anti-inflammatory.

At the end of the workshop, students will be able to adjust different parameters in order to tune the physicochemical properties of the resulting solids.

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Hybrid organic-inorganic composites for photocatalytic enviroment remediation

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In recent years, photocatalysis has experienced a continuous development, in the main applications and in the depollution of the environment. Natural photocatalytic phenomena, including plant photosynthesis, are processes known in prehistoric times without information on the intrinsic chemical mechanisms of plant growth. The artificial photocatalytic phenomenon is known from the first studies of the photochemical process. The term "photocatalysis" appears since the 1930s after which it became established in the scientific literature. The term was taken to represent a field of chemistry based on catalytic reactions that take place under the action of light. Consequently, all phenomena involving simultaneously photochemical processes and catalysis were considered to belong to photocatalysis. In the early 1970s, photocatalysis was considered an interesting alternative for the decomposition of water into hydrogen and oxygen using UV solar energy. But expectations were not met immediately, so new challenges for photocatalysis emerged in the early 1980s. The problems related to the depollution of the environment in a "green" way indicated the photocatalysis as a possibility to offer efficient solutions. Although there have been several applications of this case in the case of chemical syntheses, the main application of photocatalysis remains the degradation of environmentally toxic compounds.

As seen, photocatalytic degradation of pollutants under UV light is effective but the energy consumption is still high compared to visible light and natural light source, accounting for the energy required to power de UV lamps (UV accounts for only 4-5% of the solar spectrum) and also for the cooling systems for these lamps. Moreover, the most used semiconductors as TiO_2 suffer of some drawbacks as fast electron-hole recombination, To overcome these drawbacks, recent research focuses on the development of visible light active photocatalyst (nanomaterials like nanomembranes, nanoparticles, nanopowders, or nanocomposites) for degradation of chemical compounds and biological substances that contain heavy metals, algae, bacteria, viruses, organics, nutrients, or antibiotics [1].

Recent trends in photochemistry are focused in mimicking natural supramolecular systems, organic chromophores being one of the targeted classes of compounds. Due to their poor photostability and the ease in which they undergo self-decomposition, organic photocatalysts are less common than semiconductors [2]. The organic photosensitiser reaches a singlet electronic excited state that after intersystem crossing can reach the triplet state [2]. These excited states are stronger electron donors (the excited electron occupying a high energy orbital) or electron acceptors (accepted in the semi occupied low-energy orbital) than the ground state and thus they can participate in electron transfer processes [2]. If the organic molecule reacts with an electron donor or acceptor substrate charge separation can occur similar with semiconductors.

Metallophthalocyanines (Pcs), porfirine derivatives, can act as electron donors upon photochemical excitation in the visible region of the solar spectrum [2]. Metallophthalocyanines (MPcs) exhibit also high quantum yields for the photochemical generation of excited long lifetime (τ>100 μs) triplet states ($\Phi > 0.40$) [3]. Photocatalytic activity is exhibited by nonmetallic phthalocyanines or phthalocyanines containing metal ions with filled electron shells or d orbitals (Zn^{2+}, Mg^{2+}, Al^{3+}) etc [4,5]. Porphyrins are easily degradable by oxidation at the meso position and pyrrol rings, while metal phthalocyanines are structurally more robust and much less prone to undergo oxidative degradation [6]. However, the use of bare (metallo)phthalocyanines is limited due to recovery and stability problems. Therefore, immobilization of this kind of complexes represents a viable alternative making the shift from homogeneous to heterogeneous catalysis, preserving the desirable characteristics of both systems, high activity and selectivity (typical for homogeneous catalysis) and easy separation and recovery of the catalysts (typical for heterogeneous catalysis) TiO_2 immobilized phthalocyanines [7] or mechanical mixtures of metallophthalocyanines and zeolites [2] have been found effective for the photocatalytic degradation of organic compounds. Encapsulation of these complexes in porous supports led to an increase of activity compared with the free complex in several photocatalytic reactions attributed to two factors: concentration of substrates around active centers and a protection against degradation [8,9]. Among other applications, encapsulated (in zeolites or in porous silica or titano-silica) MPcs demonstrated photocatalytic activity in the degradation of harmful compounds to humans and environment as neurotoxic or vesicant agents [10]. Moreover, it was demonstrated that encapsulated phthalocyanines can generate singlet oxygen [11].

Encapsulation of metallo-phthalocyanines in layered double hydroxides (LDHs) represents one way to approach this concept and to create hybrid organic-inorganic supramolecular systems. Metalophthalocyanines anchored on hydrotalcites (LDH) proved to be efficient in removal and degradation of beta-lactam antibiotics from water. The immobilization of macrocyclic complexes on a well recyclable solid support such as an LDH enhances the application of such complexes for environmental pollution control. Anionic phthalocyanines (sulfonated phthalocyanines) can play the role of the charge neutralizing anion, and immobilization of the Pc complex by intercalation into a LDH host substantially improves supramolecular catalyst's reactivity, recoverability, and stability in catalytic oxidations or photocatalytic applications under Vis irradiation. The composites obtained combining the anchored MPcs and magnetic nanoparticles can provide solutions both for removal of pollutant and separation of catalyst from the reaction environment. Magnetic nanoparticles (MNPs) have got increased attention in academics, research as well as industrial fields due to its properties like high surface area, high degree of chemical stability, high catalytic activity, nonswelling in organic solvents, easily recoverable by an external magnet, reusability [12], regular shapes, uniform size, low cost of production, non-toxicity and biocompatibility.

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Proteins from marine side streams

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Processing of seafood generates large amounts of side streams or rest raw materials. It is estimated that in industrial fish filleting only about 30-50 % of the fish is made into fillets. The rest is side streams or rest raw materials. These are often used for low value applications such as feed or are even composted or wasted. The side streams contain valuable fractions like high value proteins and lipids with a high content of omega-3 fatty acids as well as minerals and bioactives. The world population is increasing and there is a need for more high value proteins. Most of the fish stocks are already fully utilized or even overexploited and there is therefore a need to use the whole catch/harvest. Protein rich side streams include heads, backbones (frames), cut-offs, skin and also viscera. Different processes are used to extract the proteins – from producing fish meal to protein hydrolysates. In recent years, production and industrial use of fish protein hydrolysate (FPH) have increased rapidly. Enzymatic hydrolysis is mostly used to extract proteins, peptides and amino acids, but also fish oil is extracted. One interesting protein that can be produced from fish side streams is gelatin. Only a small proportion of gelatin is produced from fish (*ca*. 1%). This is due both to lack of stability in supply of high quality raw material as well as the suboptimal properties of the obtained gelatin. Gelatin from cold water fish has a lower melting point and results in gels with poorer mechanical properties compared to mammalian gelatin. An overview of the different processes for protein extraction will be given in the lecture.

Agoprene - A sustainable alternative to oil-based foam.

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Agoprene is a startup company, founded by masters students at NTNU in 2020. Agoprene develops furniture foam (similar to PUR/ Polyurethane) from plant fibers found in seaweed and wood, to help the furniture industry reduce their need for petrochemicals.

Globally, furniture foam, which is derived from petroleum, accounts for 105 million tonnes of CO2 emissions annually. One armchair, for example, emits an average of 43 kg CO2e, almost half of which is due to furniture foam.

Agoprene's foam is completely free of petrochemicals. The founder of Agoprene will in this session talk about Agoprene and her belief that finding planet-friendly alternatives isn't a challenge; it's an opportunity.

Use of sidestreams to produce biodegradable plastics in a circular economy perspective

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Polymer properties such as mechanical strength, flexibility and durability have made plastics an indispensable material in our everyday use. However, polymers also create several environmental problems. Their transfer to landfill determines the depletion of the same increasing disposal costs. Their combustion leads to toxic substances and finally greenhouse gases contribute to pollution and climate change. The products produced by fragmentation (micro- and nanoplastic particles) have been found in many parts of the world, especially accumulated in the oceans where they have contaminated the food web taking hundreds of years to biodegrade in the environment. The plastics industry (e. g. in the packaging sector) is currently based on a largely linear flow of materials. This economic system is founded on around 95% fossil raw materials and has negative consequences for the environment and climate, especially without efficient recycling and energy-efficient extraction of raw materials and their processing. The growing demand for plastics, in combination with the long time needed for their biodegradation, emphasizes the need to reduce the use of different plastic materials and replace them with degradable bioplastics produced through sustainable processes. Bioplastics which can be produced from biomasses (e. g. corn, sugars and potatoes) have several advantages like a lower carbon footprint, the potential for greater independence from fossil sources, higher energy efficiency and environmental sustainability. However, at present they have higher manufacturing costs, recycling problems and very often a low mechanical resistance. Degradable bioplastics can be used to make objects that fully degrade to minimize their environmental impact. Plastics can be fully degraded to carbon dioxide and water in industrial composters, soil and water without releasing toxic by-products.

Alginates – Physiochemical properties and state-of-the art applications

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Alginates comprise a family of marine polysaccharides produces by marine brown algae [1], and some bacterial species [2, 3]. Alginate is a linear polysaccharide comprised of 1,4-linked β-D-mannuronic acid (M), and its C-5 epimer α-L-guluronic acid (G) [4]. M- and G-blocks are interspaced by MG-blocks, and the content and distribution depend both on the source and growth conditions. G-blocks adopt a $^1C_4$ chair conformation, and consequently high charge density and cavities are characteristic of G-blocks. The G-blocks cross-link certain divalent cations (Ca^{2+}, Sr^{2+}, Ba^{2+}), the interaction is described by the egg-box model, wherein the cation is complexed within the cavities of the consecutive guluronate residues [5]. The inherent ion-binding properties of G-rich alginates form the basis of their ability to form hydrogels. Alginate-based hydrogels have multiple applications including gelling, water binding, and tuning of viscosity, and has been widely explored in the pharmaceutical-, food- and biomedical industry [6].

Alginate-based nanoparticles has, as opposed to microparticles, been minimally described. Recently, alginate was incorporated in linear diblocks polymers with dextran, and upon stimuli by divalent cations, well-defined nanoparticles (< 30 nm) were formed [7]. The nanoparticles have an ionically complexed oligoguluronate core, and an outer stabilizing dextran corona. The size and stability of the nanoparticles could be tuned by the chain length of the constituent blocks, as well as the ion used for the assembly (Ca^{2+}, Sr^{2+}, Ba^{2+}). Alginate nanoparticles add to the value of alginates when considering potential applications, and in the future, biopolymers in general are envisioned to be an excellent alternative to petroleum-based polymers for the preparation of functional materials.

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Nanocelluloses in tissue engineering – effects of surface chemistry

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Lately, traditional cellulosic materials have been introduced for tissue engineering uses by extracting cellulose at nanoscale. The nanocellulose family includes wood-based cellulose nanofibrils (CNF) and bacterial nanocellulose (BNC). Compared with conventional biomaterials, nanocellulose has several advantages, such as high specific surface area, shear thinning properties, surface chemical reactivity and good mechanical properties. Biomaterials without microbial or animal-derived components are preferred immunologically, thus interest in wood-based CNF has grown recently. Isolation of CNF utilizing 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO-oxidation) has been used to introduce different functional groups and charges to the surface of CNF. Cell interaction with biomaterials is thought to be dependent on the biomaterial surface properties in general and its surface chemistry in particular. For example, the incorporation of carboxymethyl group into CNF did not promote cell adhesion and proliferation. On other hand, the partial substitution of hydroxyl groups through the TEMPO-oxidation by carboxyl and aldehyde groups resulted in enhanced stem cell adhesion, morphology, and proliferation. The aldehyde groups can be removed by oxidation to carboxylate groups using $NaClO_2$, or reduction to alcohols using $NaBH_4$. The influence of the surface chemistry of wood-derived CNF materials on different cells cytocompatibility in terms of cell viability, morphology, proliferation, and osteogenic differentiation is demonstrated. By the choice of surface chemistry, various cell responses can be promoted. CNF materials have a great potential for bone tissue engineering applications.

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Biomass residues: from well-defined properties to potential applications

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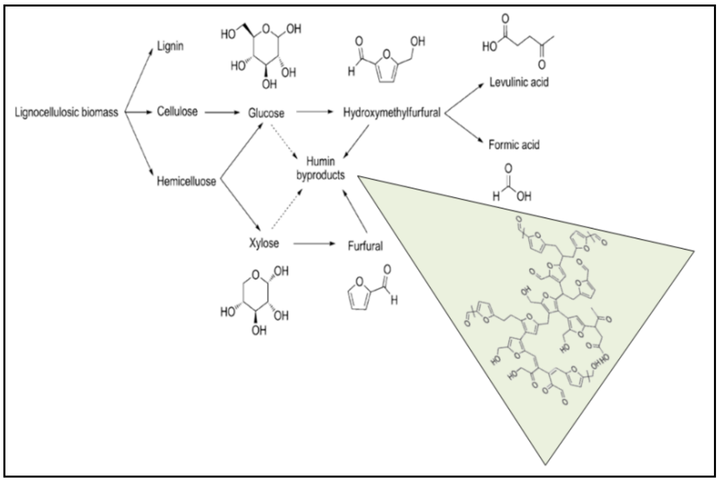
Introduction

It is widely acknowledged that there is a growing research efforts aiming to developed new processes based on residual biomass (solid, liquid and gaseous) as a renewable source for bio-productions, with environmentally acceptable in the chemical industry [1,2]. Also, it's considered carbon neutral as they do not contribute additional carbon dioxide to the atmosphere [2]. However, recycling of those materials are necessary to avoid environmental consequence due to improper disposal. In this context, lignocellulosic biomass (ie, cellulose and hemicellulose) is considered as promising alternative feedstocks for biobased chemicals and fuels [3]. Nevertheless, during the acid catalyzed treatments of lignocellulosic biomass (ie, hydrolysis to glucose or xylose) are accompanied unavoidable byproducts formed under hydrothermal conditions, which generate black solid residues, denoted as "humins", via irreversible aldol condensation among intermediates and products (Scheme 1). [4].

The chemical structure of humins mainly are made up by furanic networks linked each other by alkyl chains with several oxygen based moieties such as hydroxyl and carbonyl groups (Scheme 1) [5].



Scheme 1: Production of platform molecules from residual biomass and the related formation of humins co-products by polymerization of sugars and their intermediates [5].

Evidently, it's unlikely that humins formation can be a completely eliminated; this is leading to lower the economic value of the biochemicals production. In addition, the implementation of the circular economy (CE) is becoming imperative given the awareness of limited resources and need of environmental protection [6]. For this reason, in order to improve the efficiency of the acid-catalyzed conversion of sugars and to enhance the economic value of the process, the formation of humins should be eradicated, As such; there is an incentive to convert these humins into valuable chemicals [3] or to production of functional materials. Studies focusing on such applications are still scarce.

In this work, we aim to present one-pot dehydration of glucose to HMF in biphasic systems over niobia-based catalysts used a humins (by-products biomass treatment) as a support. Herein, we showed an example for a novel strategy used humins as a functional material, which can give a value to sustainable economy development.

Experimental

Catalysts containing 1.2 (2.5wt%) and 1.7 (3.5wt%) mmoles of Nb were prepared by a deposition precipitation-carbonization (DPC) method. Ammonium niobate(V) oxalate hydrate and humins obtained from the acid dehydration of glucose were used as precursors for niobium species. The prepared catalysts were denoted as GHNb1.2 and GHNb1.7, respectively. The resulted catalysts were exhaustively characterized by XRD, DLS, TG-DTA, DRIFT, NH_3-, CO_2-TPD, XPS and SEM-EDX techniques. The activity tests were carried out in a batch mode as follows: 0.05 g of catalyst was added to a solution of 0.18 g glucose in water. After closing, the reactor was heated at 160-180°C, under stirring for 6-12 h. Under similar conditions, additional catalytic tests were carried out in a biphasic solvent resulted from an aqueous solution of 20% NaCl and an organic solvent as 2-sec-butylphenol (SBP), 2-tert-butylphenol (TBP) or methyl-isobutyl-ketone (MIBK).

Results and discussion

After calcination, the characterization results confirmed the presence of highly dispersed niobia particles anchored onto the graphite-like carbon carrier. The distribution of niobium species on the carrier surface makes the difference between an efficient and a less-efficient catalyst. Thus, for the same concentration of surface niobium (ie, 2.4at% from XPS analysis), a relatively more homogeneous distribution (SEM analysis) of the -Nb-OH and Nb=O species (DRIFT analysis) led to an efficient catalyst while its agglomeration in relatively rich areas determined an appreciable decrease of the HMF yield. The relative base/acid sites ratio (determined from CO_2- and NH_3-TPD) is influenced by the distribution of niobium and the formation of Nb-rich particles.

The most important results collected from the catalytic tests are presented in Figure 1. As it shows, in the absence of niobia, the calcined humins generated no HMF in reaction products (Figure 1, calcined GH). This behavior might be attributed to a low concentration of weak surface acid/base functional groups in the graphite-like carbon structure. Also, no HMF production has been determined in pure water or TBP (Figure 1), presumably due to the inhibition rate as an effect of a fast rehydration to furan ring opening products (levulinic and formic acids). Replacing the monophasic solvent with a bi-phasic TBP/water, HMF started to accumulate (Figure 1) and a yield of 16% HMF was determined in reaction products. However, the presence of NaCl in the aqueous phase plays an important role in improving the partition coefficient of HMF. Indeed, in the bi-phasic TBP/water system with 20%NaCl in the aqueous phase, the yield to HMF had an very important increase, jumping from 16 to 96% (Figure 1).

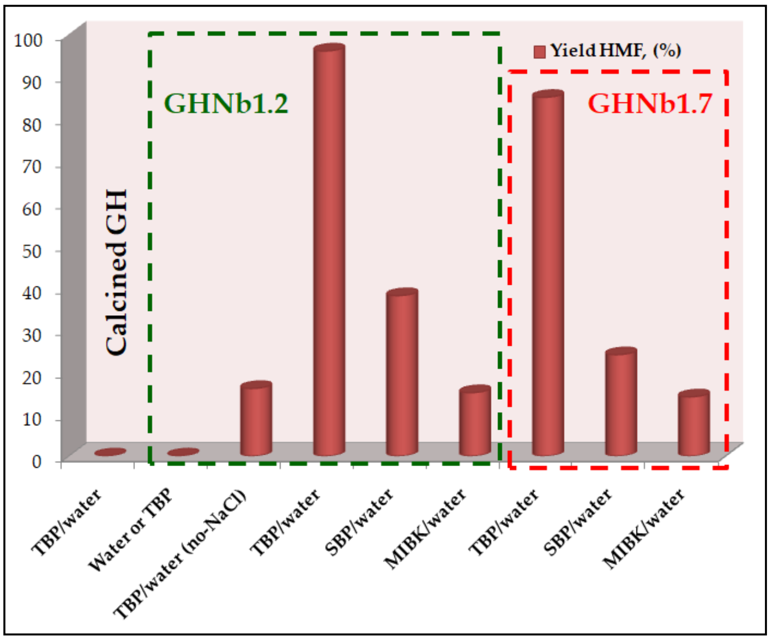


Figure 1: Catalytic results in glucose dehydration to HMF in biphasic systems; *Reaction conditions: 0.18g D-glucose, 50mg of catalyst, solvent [3.5ml* H_2O *(NaCl 20%) + 1.5ml extracting solvent], reaction temperature: 180 ℃, reaction time: 8h, 1000 rpm*

Under the same experimental conditions, taking GHNb1.7 as catalyst, the trend was similar but the yields were smaller than those obtained with GHNb1.2 (Figure 1). These results confirm the importance of the base/acid ratio in this reaction. As XPS measurements showed, the concentration of superficial niobium was similar for both GHNb1.2 and GHNb1.7 catalysts while the TPD measurements evidenced a much higher base/acid sites ratio for GHNb1.7 (4.25). However, GHNb1.7 led to lower yields in HMF indicating that a high HMF yield requires an optimum base/acid sites ratio. For the moment such a condition is fulfilled for GHNb1.2 with a ratio of 1.76.

Conclusions

Obtained results show that humins (by-products of renewable biomass-based technologies), may offer valuable solutions for the production of functional materials with catalytic application. The preparation procedure induced structural modifications of the humins carrier with the formation of a highly hydrophobic graphite-like carbon structure and acid-base functionalities, on which niobium is dispersed on. These structural features are responsible for the high yields to HMF.

Acknowledgements

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A green approach for the synthesis of CQD@ZnO nanocomposites with superior photocatalytic properties

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Introduction

Photocatalysis is a promising route to offer answers to the increasing environmental and energy concerns [1]. This well correlates to the development of new photocatalysts materials able to shift the adsorption range from UV towards the visible one [2]. In this context, ZnO has received significant attention, due to its high photosensitivity, non-toxicity, low cost, high exciton binding energy, and competitive photocatalytic activity [3]. ZnO is thus largely investigated for removing environmental pollutants related to wastewater, polluted air, and spilled water [3]. However, the large bandgap of ZnO (3.37 eV), the massive charge carrier recombination and the photoinduced corrosion–dissolution at extreme pH conditions, together with the formation of inert Zn(OH)$_2$ during photocatalytic reactions act as barriers for its extensive applicability. Therefore, intensive research has been done to improve the performance of ZnO by tailoring its surface-bulk structure and by altering its photogenerated charge transfer pathways with an intention to inhibit the surface-bulk charge carrier recombination.

Despite the numerous reports on the synthesis and the simultaneous efforts made to exploit CQDs for various applications, the synthesis of CQD@ZnO nanocomposites was investigated only in a few reports with the aim to promote ZnO photocatalytic activity under visible light irradiation [4].

Herein, we developed a green simple route to prepare CQD@ZnO nanocomposites using a low-temperature hydrothermal approach. The method involves CQDs obtained from useless humins waste. The photocatalytic properties of synthesized CQD@ZnO heterostructures were investigated in the degradation of methylene blue (MB), a representative of a class of dyestuff resistant to biodegradation.

Experimental

CQDs aqueous solutions were prepared by the low-temperature hydrothermal degradation of humins at 180°C for 12 h (CQD$_{180-12}$) and at 200°C for 4 h (CQD$_{200-4}$). Two processes were used to prepare CQD@ZnO nanostructures: (1) the hydrothermal approach, in which commercial ZnO was slowly added to a solution of CQDs and kept at rt for 4 h and then heated at 140 °C for 4h, and (2) the one-pot hydrothermal approach, in which $Zn(CH_3COO)_2 \cdot 2H_2O$ was dissolved in the CQDs solution at rt. The pH was adjusted with NaOH aqueous solution (8 M) and vigorously stirred for 15 min at rt and then at 80°C for 3 h. Irrespective of the applied approach, the final CQDs@ZnO products were collected by centrifugation, washed and dried in air for 12h at 80 °C.

Obtained CQDs@ZnO were characterized by adsorption-desorption isotherms of liquid nitrogen at 77 K, XRD, DRIFT spectroscopy, and UV-VIS spectroscopy.

The photocatalytic performance of the CQD@ZnO nanocomposites was evaluated using a pollutant model, methylene blue (MB), under UV and visible light irradiation.

Results and discussion

The roles performed by CQDs may differ according to the region of light irradiation. In ultraviolet (UV) region, CQDs display electron-sink behavior which helps in trapping scattered electrons released by metal oxides. Therefore, the photocatalytic efficiency of CQD@ZnO nanomaterials intensely depends on the CQDs presence. However, the ZnO morphology and the particles size have also an important role as the results suggested in the MB photodegradation (Figures 1 and 2).

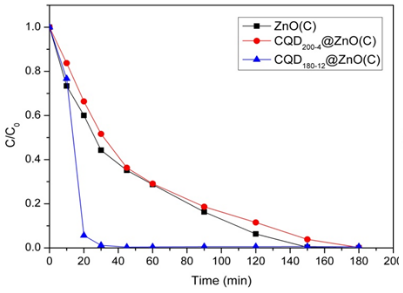

Figure 1. The degradation of MB (665 nm band) in time in the presence of CQD@ZnO(C) samples and under UV irradiation

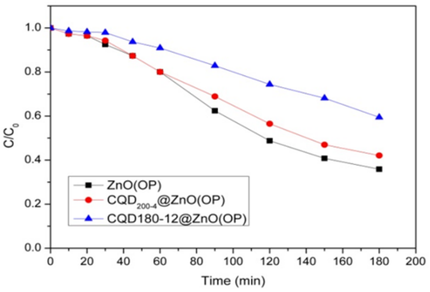

Figure 2. The degradation of MB (665nm band) in time in the presence of CQD@ZnO(OP) samples and under UV irradiation

Even if, generally, the degradation of MB takes place at a lower level, the obtained results clearly indicate a successfully degradation of MB also under Vis irradiation. The main factors which contributed to this degradation are the morphology of the ZnO, the presence of the CQDs and the pH of the liquid phase. The best results were obtained in the presence of CQD_{180-12}@ZnO(C) sample.

Conclusions

The presence of CQDs on the surface of ZnO can promote the range of spectrum absorption from UV into visible. The CQDs also act as electron reservoirs that resist the recombination of electron-hole pairs. However, the increased photocatalytic activity of CQDs@ZnO can be obtained with smaller CQDs size (i.e., CQD_{180-12}). Both the photodegradation mechanism and the correlation of the catalytic properties-catalytic efficiency will be discussed.

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Selective HMFCA production over Co-based MOFs catalysts

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Introduction

With the current transition state of the industry towards sustainable development, biomass valorization rises as the only viable option to achieve this goal. From the large spectrum of molecules that can be generated from biomass, the furanic compounds are a bountiful feedstock for the production of chemicals, fuel-additives and biofuels [1]. 5-Hydroxymethyl-2-furancarboxylic acid (HMFCA), for example, is obtained from the incomplete oxidation of 5-hydromethylfurfural (HMF) and is an important building block for both polymer and pharmaceutical industries [2]. However, only a few studies focus on the targeted production of HMFCA by applying stoichiometric, catalytic or biocatalytic oxidation, each of these approaches having some drawbacks but the same major challenge: the easy over-oxidation towards the dicarboxylic acid [3]. Nevertheless, it is preferred to employ heterogeneous catalysis which brings advantages like easy recovery, recyclability and possibly more sustainable reaction conditions.

Metal-organic frameworks (MOFs) are a class of hybrid organic-inorganic materials, renowned for their structural properties, particularly their tunability and easy design [4] which makes them good candidates for gas storage as well as for catalysis. Since their discovery, MOFs have known a continuous growth and interest, with a large number and diversity of structures existing nowadays, many of which embrace the water- and thermal stability. Thus, expanding the MOFs application, especially in biomass upgrading processes as promising alternatives to classic solid catalysts is expected [5].

In this context, the aim of the present study was to develop Co-based MOFs catalysts able to combine a high catalytic efficiency with a high hydrothermal stability in the selective HMFCA production from renewable HMF using t-BuOOH as oxygen donor and acetonitrile as solvent.

Experimental

Four different Co-based MOFs samples, i.e. Co-BTC@Co3O4, Co-BTC, Co-BTC-2mim and ZIF-67 were prepared and characterized through XRD, liquid nitrogen adsorption-desorption isotherms, TG-DTA, CO2- and NH3-TPD, DRIFT spectroscopy and SEM.

The catalytic experiments were carried out in a stainless-steel autoclave in following conditions: to a solution of 25-100 mg HMF in 4.4 mL acetonitrile (ACN), 50-180 µL t-BuOOH (70 wt%) and 5-25 mg Co-based MOF catalyst were added. The resulted mixture was stirred at 20-100°C for 1-24 h. After reaction the catalyst was recovered by filtration and the products were separated by solvent distillation under vacuum. Recovered products were silylated, diluted with ethyl acetate and analyzed with a GC-MS (THERMO Electron Corporation) equipped with a TG-5SilMS column.

Results and discussions

The screening of the catalysts in the HMFCA production using t-BuOOH as oxidation agent, in acetonitrile as solvent, at 60⍰C and 1h, indicates the Co-BTC@Co3O4 sample as the most efficient in terms of HMF conversion (79.3%) and HMFCA selectivity (82.1%) (Figure 1). Very important, recyclability of the Co-BTC@Co3O4 catalyst, revealed a slightly decreased of HMF conversion from 79.6 to 74.7% and an upward trend from 87.6 to 92.7% for the selectivity to HMFCA. The observed variations could be related to the gradual release of water molecule during the recovery reactions. Besides, no obvious difference for both the fresh and recovered samples was observed in XRD pattern (Figure 2), indicating the sample was stable during the liquid reaction.

To explain the obtained results the structural and chemical characteristics, such as morphology, metal node coordination and acidity/basicity of the Co-based MOFs will be discussed and correlated with their catalytic efficiency.

Conclusions

A range of acid-base Co-based MOFs materials were successfully prepared and demonstrated to be efficient for the HMF selective oxidation to HMFCA. However, the best catalytic results were obtained in the presence of Co-BTC@Co3O4 sample. Not less important the developed materials are highly stable in the used reaction conditions. Both the oxidation mechanism and the correlation of the catalytic properties-catalytic efficiency will be discussed.

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A circular economy concept: from biomass wastes to CQD/TiO2 catalysts with enhanced photodegradation efficiency of organic dyes

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Introduction

Photocatalytic reactions driven by sunlight represent a promising way to address the increasing environmental and energy concerns. To date, various photocatalytic semiconductors were used to improve the visible light assisted reactions. However, by far, titanium dioxide (TiO2) is the most studied due to its abundance, low cost, low toxicity, great photostability, and high intrinsic catalytic activity under UV irradiation [1]. Nevertheless, there are problems with the TiO2 – the poor responses to visible light caused by its wide bandgap (3.0–3.2eV) and the fast recombination of photogenerated electron-hole pairs. In this way, its application in photocatalysis were limited [2]. As to improve the photocatalytic properties of the TiO2 a combination with carbon structures was investigated. Particularly, Carbon Quantum Dots (CQDs) were used to address the problem of the wide bandgap. The induced modifications are controlled by the CQDs dimensions [3].

Here we present the development of CQD@TiO2 nanocomposites with potential photocatalytic activity in the purification of waste waters. For testing the activity of the new material, methylene blue (MB), an example of dyestuff resistant to biodegradation, was used.

Experimental

An eco-friendly low-temperature hydrothermal decomposition of humins (i.e., insoluble, polyfuranic polymers, by-products obtained from D-glucose acid-catalyzed dehydration [4]) at temperatures of 160–200 ⍰C, for 4-12 h, was applied for CQDs synthesis (denoted CQDT-h). The new nanocomposites (CQDs@TiO2) were obtained via a hydrothermal method, following a reported methodology [5]. The prepared materials were exhaustively characterized by adsorption-desorption isotherms of liquid nitrogen at 77K, XRD, elemental analysis, TG-DTA, DRIFT spectroscopy, UV-vis spectroscopy, SEM, TEM and STEM-EDS. For MB degradation, blue LED lamps (112W), emitting at 445-465 nm, and red LED lamps (112W), emitting at 630-650nm, were used as light source. To reach the adsorption equilibrium all the systems were kept in darkness, for 15 min, prior illuminating. The dye concentration was determined from a standard curve using the absorbance values measured by the UV–visible spectrophotometer (SPECORD 250-222P108), which was adjusted at 664 nm (wavelength corresponding to the maximum absorption of MB).

Results and discussion

The XRD patterns of the CQD@TiO2 samples did not show diffraction lines characteristic to CQDs, indicating their small loading weight, poor crystallinity, small size and their high dispersion in the new material. This is also confirmed by STEM analyses which evidenced the presence of ultra-small CQDs particles on the TiO2 surface, with a size of 2 nm, for CQD200-4 and 8 nm for CQD180-12. The presence of the CQDs on the surface of the TiO2 was also confirmed by DRIFT analysis which evidenced the presence of bands corresponding to –COOTi- group. These results suggest a direct connection of CQDs and TiO2 through a heterojunction enabling photoexcited charge carriers.

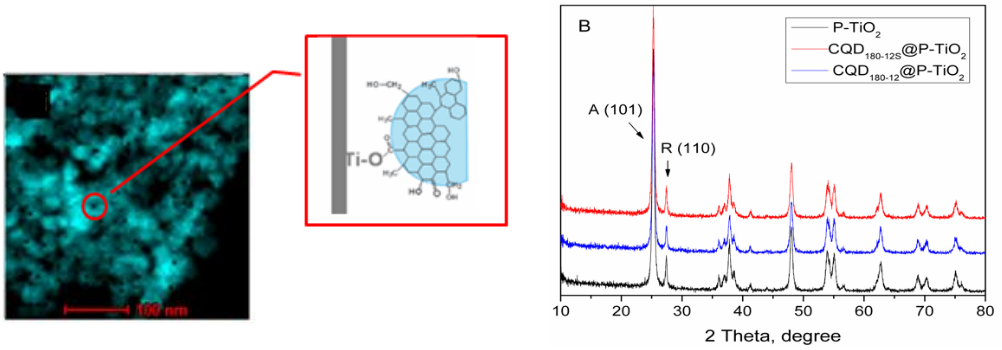

Figure 1. STEM image of CQD180-12@TiO2 sample and XRD patterns of the obtained composites.

While the MB adsorption capacity of the pristine TiO2 is limited, the presence of the CQDs enhanced the process. Accordingly, in the presence of the CQD180-12@TiO2 the adsorption of MB was 60.7% and grew to 90.6% in the presence of CQD200-4@TiO2. Furthermore, the absorbance of MB (UV-vis) changes as the reaction progress, affording its gradual degradation under visible light radiation. Therefore, MB was degraded in only 60 min in the presence of CQD180-12@TiO2 sample.

Conclusions

As to conclude, new photocatalytic composites for the MB dye degradation were successfully synthesized. CQDs act as photosensitizers to narrow the bandgap of TiO2 and enlarge the absorption range capability of TiO2 into the visible light region. CQDs act as electron donors, transferring photo-generated electrons to the VB of TiO2 providing more electrons for the degradation process and enhancing the separation of photo-generated electron–hole pairs. The heterointerface also contributes to their separation. All these aspects will be presented and discussed in detail.

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Bifunctional Ru/Beta zeolite catalysts for the biomass feedstock upgrading

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Introduction

Resource-efficient production of fuels and chemicals, conserving feedstock and energy, is a key challenge for the sustainable development of the chemical industry and human society. In line with this, high efforts of the global academic and industrial research are nowadays directed toward the utilization of non-food biomass-based feedstocks (ie, lignocelluloses) to make chemical precursors that are either petrochemical equivalents or new ones to make everyday products (e.g., plastics, synthetic fibers, detergents, transportation materials and the like) [1]. However, selective conversion of biomass to desired products, meeting the requirements of green chemistry and engineering, still remains a challenge. Catalysis meets all these requirements being recognized as one of the most important tools for implementing green chemistry. Therefore, it is not incomprehensible the major research effort focused on the upgrading of lignocelluloses biomass, in which the major task is to selectively remove or introduce functional groups from/to the feedstock molecules, using either existing, redesigned or entirely novel catalysts [2]. Catalytic hydrogenation in biomass valorization is one of the most significant example for which the effective design of suitable catalysts still represent a significant challenge due to: 1) the conversion processes which involve multistep reactions and 2) the poor intrinsic reactivity of carboxylic acid group. The selective hydrogenation of carboxylic acids, such as levulinic acid (LA) and succinic acid (SA) [3] is a good example in this sense.

Zeolite-based catalysts are of great interest in the actual chemical industry but also have a high potential for upgrading in the future bio-based chemical industry, owing to their intrinsic properties and especially in view of their extraordinary versatility. Moreover, the deposition of metals in form of nanoparticles onto the external surface of zeolites enables to generate catalysts featuring both strong acid and redox sites [4]. The use of such bifunctional material is advantageous to perform a two-step reaction in one pot.

In this context, the aim of this study was to develop a series of bifunctional Ru-based Beta zeolites (Si/Al= 12.5, 18.5 and 150) as potential catalysts for the selective hydrogenation of levulinic acid to 2-methyltetrahydrofuran and 1,4-pentanediol and of succinic acid to 1,4-butanediol. Herein will be presented some results obtained in the catalysts preparation and their XRD characterization.

Experimental

A serie of Ru-based zeolite catalysts with 1, 2, 3 and 5wt% Ru and Beta zeolites with Si/Al = 12.5, 18.5 and 150 as carriers were prepared by wet impregnation. In a typical procedure, an aqueous solution with a corresponding amount of $RuCl_3$ was added dropwise and under stirring to a suspension of zeolite in water. The obtained slurry was further stirred for 24h at room temperature. Aster impregnation, the solid was separated from liquid phase by centrifugation (at 6000 rpm for 35-40 min), dried under vacuum, calcined at 450°C for 4h and reduced either in a H_2 flow at 350°C for 1h or with $NaBH_4$, at room temperature for 4h. Obtained samples were characterized by XRD, adsorption-desorption isotherms of liquid nitrogen, DRIFT spectroscopy, and CO_2- and NH_3-TPD analysis.

Results and discussions

Figure 1 displys the XRD patterns for Ru/Beta zeolite samples with Si/Al = 150. The characteristic sharp and intensive reflections of H-Beta zeolites, at 2θ values of 7.6, 21.2 and 22.4° were consistent with the typical diffraction lines of the referenced Beta zeolite, indicating a well-developed crystalline structure of Beta topology, formed by the intergrowth of polymorphs A and B [5]. Reflections of metallic hexagonal Ru associated with (010), (002), and (011) planes are clearly visible at 2 theta values close to 38, 41, and 43° (ICDD-JCPDS Card No. 06-0663), respectively, while tetragonal RuO_2 diffracting along the (110), (011), and (121) planes was found at 2 theta values of 28, 35.1, and 54° (ICDD-JCPDS Card No. 43-1027), respectively [6]. The intensities of the diffraction lines for Ru-Beta samples are smaller than for the Beta zeolite carrier, indicating that these catalysts contains more amorphous phase. A lower crystallinity of Ru-Beta is due to the alkaline treatment causing amorphization, analogously to the work of Verboekend et al. [7]. Figure 1 also shows a visible difference between Ru-based samples, in terms of ruthenium reduction degree and particle size, as a function of the ruthenium concentration.

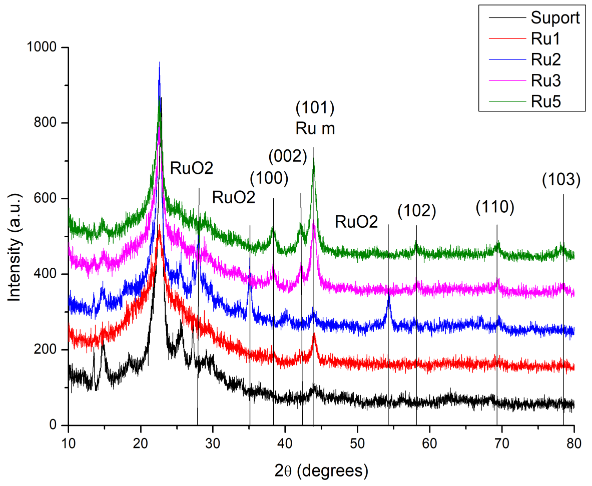

Fig 1. XRD pattern for Ru1%, Ru2%, Ru3% and Ru5% loaded samples on beta zeolite (Si/Al=150)

Conclusions

The XRD characterization of the Ru-based Beta zeolites confirm the successfully preparation of bifunctional Ru-based catalysts. The main characteristic features of the prepared samples will be discussed by correlating the results obtained from all applied characterization techniques. Catalysts will applied in the hydrogenation of levulinic acid and of succinic acid.

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Posters 1-6

Poster # 1

Biomass-derived graphene and its oxide used to design heterogeneous chiral catalyst for the Henry, cyanosilylation and aldol coupling reactions

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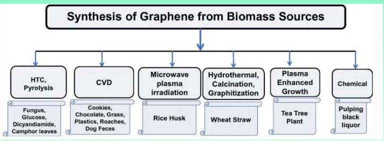
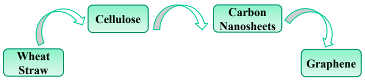
Abstract: As the most value-added carbon nanomaterials, graphene and carbon nanotubes (CNTs) have been widely studied and employed in a diverse assortment of applications due to their unique and impeccable structures. Recent advances in biomass-derived graphene and CNTs with a focused on manufacturing high-quality graphene and CNTs from a range of disparate biomass materials and their applications in electrochemistry, catalysis etc. The biomass-derived graphene and CNTs demonstrate new avenues of innovative ecosystems and opportunities. Various biomass materials, such as cotton, corncobs, and camphor leaves, have been successfully converted into graphene and CNTs[1,2]. Biomass materials often serve as both scaffolds and biocatalyst[3]. In this work, the use of graphene and its oxide form used to design a heterogeneous chiral catalysts those results excellent in catalysis. More recently, organocatalysis elicited an additional interest by offering a green alternative to metal complex catalysis through replacing the metal by organo functionalities such as amine or tio- groups. Further immobilization of such structures on biomass derived graphenes and its other moieties enlarges the advantages of these catalytic systems affording an easier separation and recycling of the catalyst. Asymmetric catalytic reactions with such systems make even more appealing their utilization. Based on this state of the art- cyanosilylation, aldol coupling and asymmetric Henry reactions were carried out with L- and D-valmet ligands in different configurations: i) coordinated to sodium ions, as organocatalysts, with week base properties, ii) complexes with copper(II), as homogeneous catalysts, and iii) immobilized copper(II) complexes onto graphene oxide (GO) as heterogeneous catalysts. For the reaction of benzaldehyde and nitromethane in water these afforded an asymmetric Henry reaction, with a spectacular increase of the conversion and ee (92 and 95%, respectively) after the deposition on GO. Ligand complexed copper was also effective for cyanosilylation and Aldol coupling reaction.

SYNTHESIS OF COMPLEXES

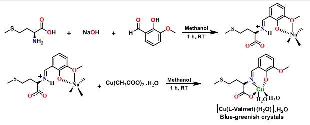

Synthesis of Graphene from Biomass Sources

- HTC, Pyrolysis: Fungus, Glucose, Dicyandiamide, Camphor leaves
- CVD: Cookies, Chocolate, Grass, Plastics, Roaches, Dog Feces
- Microwave plasma irradiation: Rice Husk
- Hydrothermal, Calcination, Graphitization: Wheat Straw
- Plasma Enhanced Growth: Tea Tree Plant
- Chemical: Pulping black liquor

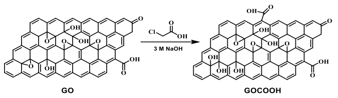
GRAPHENE SYNTHESIS


Wheat Straw → Cellulose → Carbon Nanosheets → Graphene

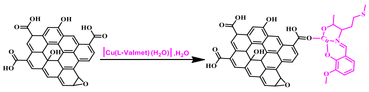
SYNTHESIS OF COMPLEX



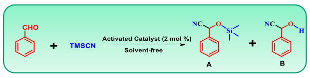
FUNCTIONALIZATION OF GO WITH ACID



IMMOBILISZATION ON GO-COOH

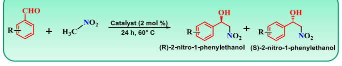


CATALYTIC ACTIVITY OF CATALYST IN CYANOSILYLATION REACTION AND HENRY REACTION



Entry	Catalyst	Time (h)	Temp. (C)	Conversion (%)	Molar ratio (A:B)
1	Cu(L-Valmet).xH$_2$O x<1	24	24	97	11.9 : 1
2	Cu(L-Valmet).xH$_2$O x<1	24	80	100	13 : 1
3	GO/Cu(L-Valmet).xH$_2$O x<1	24	24	0	-
4	GO/Cu(L-Valmet).xH$_2$O x<1	24	80	24	0 : 100

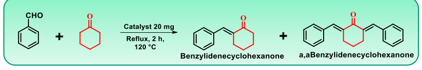
Reaction conditions: benzaldehyde (0.5 mmol) and TMSCN (Trimethylsilyl cyanide) (1 mmol), solvent free, [b] A: Phenyl-trimethyl-silanyloxy-acetonitrile and B: Benzaldehyde cynohydrin. Conversion observed with ^{1}H-NMR.



Entry	Catalyst	Solvent	Conversion (%)	ee (%)
1	L-Valmet	Water	8	98 *(R)*
2	Cu(L-Valmet).xH$_2$O x<1	Water	39	*62 (R)*
3	GO/Cu(L-Valmet).xH$_2$O x<1	Water	92	96 *(R)*
4	CuO/GO	Water	0	-
5	Blank	Water	0	-

Reaction conditions: benzaldehyde (1 mmol), nitromethane (10 mmol) and 2ml solvent. Conversion observed with ^{1}H-NMR and enantioselectivity with HPLC.

ALDOL CONDENSATION REACTION



Entry	Catalyst	Conversion of cyclohexanone (%)	Selectivity [%] 2-benzylidene-cyclohexanone	2,6-dibenzylidene-cyclohexanone.[%]
1	L-Valmet	71	19	81
2	Cu(L-Valmet).xH$_2$O x<1	48	34	66
3	GO/Cu(L-Valmet).xH$_2$O x<1	45	38	62
4	GOCOOH	39	48	52

Reaction conditions: 20 mg catalyst, benzaldehyde (2 ml) and cyclohexanone (1 ml). Conversion observed with Gas chromatography

CHARACTERIZATION OF CATALYST

FTIR spectra

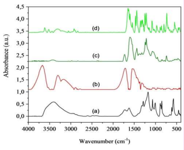


Figure 1. FTIR spectra of (a) GO, (b) GO-COOH, (c) GO-COOH/Cu(D-valmet) and (d) [Cu(D-valmet)(H$_2$O)] · H$_2$O

CD- spectra

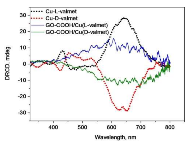


Figure 2. Copper complexes and of the hybrid chiral systems: GO-COOH/Cu(L-valmet) and GO-COOH/Cu(D-valmet)

Raman- spectra

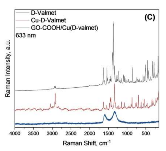


Figure 3. Copper complex and of the hybrid chiral systems: D-Valmet, Cu-D valmet, GO-COOH/Cu(D-valmet)

CONCLUSIONS

- L- and D-valmet ligands exhibit base properties and may act as homogeneous organocatalysts for aldol reaction.
- Cu-complexated by L- and D-valmet behaves as an excellent homogeneous catalyst for Cyanosilylation reaction.
- Immobilization of these complexes on GO-COOH led to a spectacular increase of the conversion with good enantioselectivity for henry reaction

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Poster # 2

UNIVERSITY OF BUCHAREST
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Selective HMFCA production over Co-based MOFs catalyts

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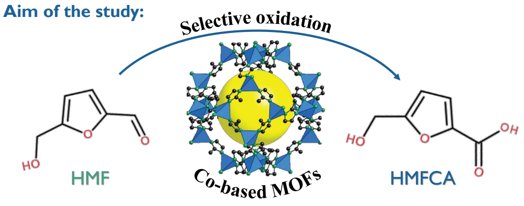
Introduction:

With the current transition state of the industry towards sustainable development, biomass valorization rises as the only viable option to achieve this goal. From the large spectrum of molecules that can be generated from biomass, the furanic compounds are a bountiful feedstock for the production of chemicals, fuel-additives and biofuels [1]. 5-Hydroxymethyl-2-furancarboxylic acid (HMFCA), for example, is obtained from the incomplete oxidation of 5-hydromethylfurfural (HMF) and is an important building block for both polymer and pharmaceutical industries [2]. However, only a few studies focus on the targeted production of HMFCA by applying stoichiometric, catalytic or biocatalytic oxidation, each of these approaches having some drawbacks but the same major challenge: the easy over-oxidation towards the dicarboxylic acid [3]. Nevertheless, it is preferred to employ heterogeneous catalysis which brings advantages like easy recovery, recyclability and possibly more sustainable reaction conditions.

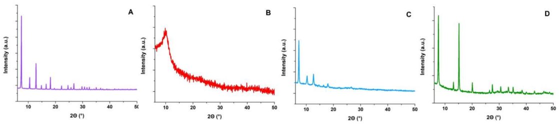
Metal-organic frameworks (MOFs) are a class of hybrid organic-inorganic materials, renowned for their structural properties, particularly their tunability and easy design [4] which makes them good candidates for gas storage as well as for catalysis. Since their discovery, MOFs have known a continuous growth and interest, with a large number and diversity of structures existing nowadays, many of which embrace the water- and thermal stability. Thus, expanding the MOFs application, especially in biomass upgrading processes as promising alternatives to classic solid catalysts is expected [5].

In this context, the aim of the present study was to develop Co-based MOFs catalysts able to combine a high catalytic efficiency with a high hydrothermal stability in the selective HMFCA production from renewable HMF using t-BuOOH as oxygen donor and acetonitrile as solvent.

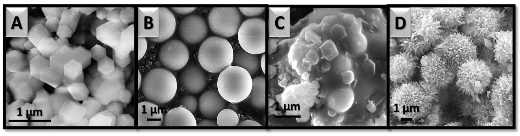
Aim of the study:



Characterization:



XRD patterns of (a) ZIF-67, (b) Co-BTC, (c) Co-BTC-2mim, (d) Co-BTC@Co_3O_4



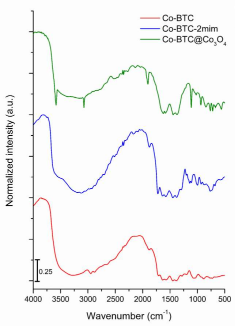
SEM images of (a) ZIF-67, (b) Co-BTC, (c) Co-BTC-2mim, (d) Co-BTC@Co_3O_4

Textural properties

Material	Specific surface area ($m^2 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)	Average pore diameter (nm)
ZIF-67	1169	0.70	2.40
Co-BTC	344	0.59	6.87
Co-BTC-2mim	167	0.12	2.83
Co-BTC@Co_3O_4	24	0.10	2.87

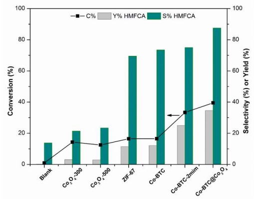
Acid-base properties

Material	Acid sites (µmol g^{-1})	Basic sites (µmol g^{-1})
ZIF-67	2.9	48.1
Co-BTC	230.9	2.7
Co-BTC-2mim	99.4	195.0
Co-BTC@Co_3O_4	16.7	139.6

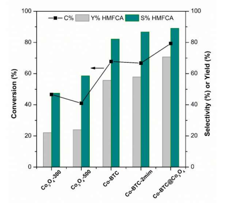


DRIFT spectra of Co-based MOFs

Catalytic tests:

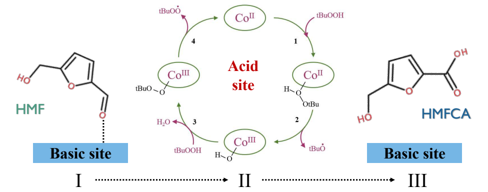


HMF conversion and selectivity/yield to HMFCA in the presence of Co-based MOF materials and Co_3O_4 oxides. *Reaction conditions: 25 mg HMF, 5 mg catalyst, 4.4 mL ACN, 75 µL t-BuOOH (70%), 60℃, 1h.*

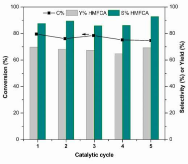


HMF conversion and selectivity/yield to HMFCA in the presence of Co-based MOF materials and Co_3O_4 oxides. *Reaction conditions: 25 mg HMF, 5 mg catalyst, 4.4 mL ACN, 180 µL t-BuOOH (70%), 60℃, 1h.*

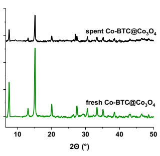
Proposed mechanism:



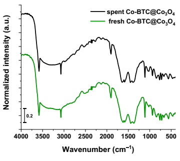
Recyclability:



Co-BTC@Co_3O_4 catalyst recyclability tests in the HMF oxidation. *Reaction conditions: 25 mg HMF, 5 mg cat, 4.4 mL ACN, 180 µL t-BuOOH (70%), 60℃, 1h.*



XRD patterns of fresh and spent Co-BTC@Co_3O_4



DRIFT spectra of fresh and spent Co-BTC@Co_3O_4

Conclusions:

- Four Co-based MOFs were prepared via solvothermal method. Each material exhibit different morphologies, textural and acid-base properties as a function of the employed metal sources and ligands.
- All four materials are efficient for the selective oxidation of HMF to HMFCA, which was carried out under weakly basic conditions ensured by the acetonitrile solvent. However, the best catalytic results were obtained in the presence of Co-BTC@Co_3O_4 sample.
- The decomposition of t-BOOH onto Co sites plays a crucial role in the oxidation of HMF, as it generates OH^- species which catalyze the formation of geminal diols and subsequently, adsorbed species on catalytic Co^{3+} sites abstract hydrogen from C-H and O-H groups of geminal diol to yield the carboxylic group.
- Recyclability tests revealed that Co-BTC@Co_3O_4 maintain its performance over 5 subsequent runs with slightly decrease of C% and an upward trend for S%.

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Poster # 3

BioMat
11-17th September 2022

Bifunctional Ru/Beta zeolite catalysts for the biomass feedstock upgrading

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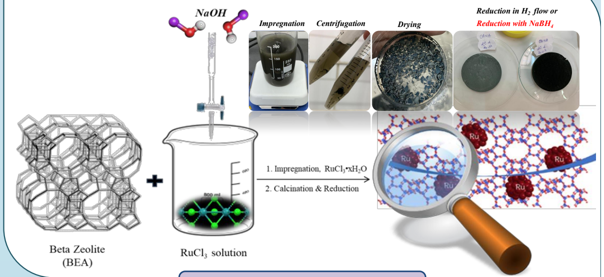
Introduction

Resource-efficient production of fuels and chemicals by conserving feedstock and energy is a key challenge for the sustainable development of the chemical industry and human society. In line with this, high efforts of the global academic and industrial research are nowadays directed toward the utilization of non-food biomass-based feedstocks (ie, lignocelluloses) to produce added value products on the consumer market (e.g., plastics, synthetic fibers, detergents, transportation materials and the like) [1]. However, selective conversion of biomass to desired products, meeting the requirements of green chemistry and engineering still remains a challenge. Catalysis meets all these requirements being recognized as one of the most important tools for implementing green chemistry. Therefore, it is not incomprehensible the major research effort focused on the upgrading of lignocelluloses biomass, in which the major task is to selectively remove or introduce functional groups from/to the feedstock molecules, using either existing, redesigned or entirely novel catalysts [2]. Catalytic hydrogenation in biomass valorization is one of the most significant example for which the effective design of suitable catalysts still represent a significant challenge due to: 1) the conversion processes which involve multistep reactions and 2) the poor intrinsic reactivity of carboxylic acid group. The selective hydrogenation of carboxylic acids, such as levulinic acid (LA) and succinic acid (SA) [3] is a good example in this sense. Zeolite-based catalysts are of great interest in the actual chemical industry but also have a high potential for upgrading in the future bio-based chemical industry, owing to their intrinsic properties and especially in view of their extraordinary versatility. Moreover, the deposition of metals in form of nanoparticles onto the external surface of zeolites enables to generate catalysts featuring both strong acid and redox sites [4].

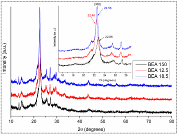
The use of such bifunctional material is advantageous to perform a two-step reaction in one pot. In this context, the aim of this study was to develop a series of bifunctional Ru-based Beta zeolites (Si/Al= 12.5, 18.5 and 150) as potential catalysts for the selective hydrogenation of LA to 2-methyltetrahydrofuran and 1,4-pentanediol and of SA to 1,4-butanediol.
Herein will be presentedsome results obtained in the catalysts preparation and their characterization.

Catalysts preparation

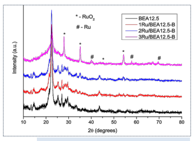


Catalysts characterization

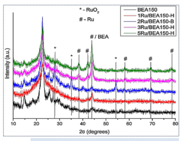
X-Ray Diffraction:



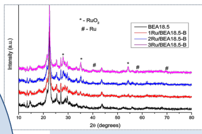
XRD patterns of BEA zeolites



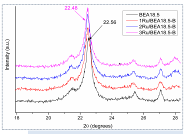
XRD patterns of BEA12.5 zeolite and impregnated samples



XRD patterns of BEA150 zeolite and impregnated samples

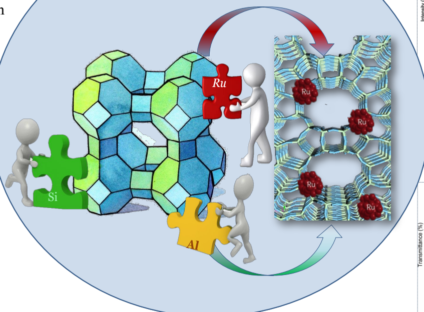


XRD patterns of BEA18.5 zeolite and impregnated samples



XRD patterns of Ru/BEA18.5 samples (2θ = 16-30° range)

Aim of the study



Adsorption-desorption isotherms of liquid nitrogen at -196℃:

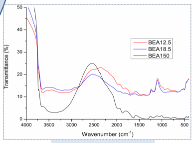
	Sample	S_{BET} (m^2/g)	S_{ext} (m^2/g)	S_{micro} (m^2/g)	V_{total} (cm^3/g)	V_{meso} (cm^3/g)	V_{micro} (cm^3/g)	V_{micro}/ V_{meso}	Pore size distribution (nm)
1	BEA12.5	**495**	186	309	**0.72**	0.58	0.14	0.24	**9.4; 31.5**
2	3Ru/BEA12.5-B	262	172	90	0.38	0.34	0.04	0.12	4.0; 9.4; 107
3	BEA18.5	**613**	188	426	**0.40**	0.20	0.20	1.0	**3.9**
4	1Ru/BEA18.5-B	460	182	278	0.39	0.26	0.13	0.5	3.9; 5.5; 50-86
5	2Ru/BEA18.5-B	416	181	235	0.35	0.24	0.11	0.46	3.9; 5.5; 50-86
6	3Ru/BEA18.5-B	381	234	147	0.44	0.37	0.07	0.19	3.5; 5.5; 45-90
7	BEA150	**497**	133	364	**0.29**	0.12	0.17	1.4	**3.8**
8	1Ru/BEA150-H	281	217	64	0.35	0.32	0.03	0.09	3.9; 9.3; 17.4; macropores
9	2Ru/BEA150-B	306	163	143	0.30	0.23	0.07	0.3	3.9; 7.6; macropores
10	3Ru/BEA150-H	421	273	148	0.38	0.31	0.07	0.22	3.9; 7.1; macropores
11	5Ru/BEA150-H	434	267	167	0.38	0.30	0.08	0.27	3.9; 7.1; macropores

Textural properties of BEA and Ru/BEA samples, where:

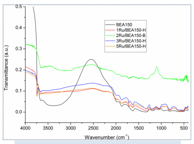
xRu/zeolite-B or xRu/zeolite-H

x is the content of the Ru (1, 2, 3 or 5 wt%), *zeolite* is BEA carrier with a certain Si/Al ratio and *B* indicates the use of $NaBH_4$ as reductant, whilst *H* indicates the use of H_2 as reductant

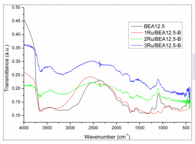
DRIFT spectroscopy:



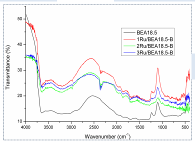
DRIFT spectra of BEA12.5, BEA18.5 and BEA150 zeolites



DRIFT spectra of BEA150, 1Ru/BEA150-H, 2Ru/BEA150-B, 3Ru/BEA150-H and 5Ru/BEA150-H samples

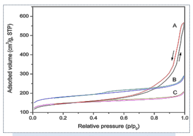


DRIFT spectra of BEA12.5, 1Ru/BEA12.5-B, 2Ru/BEA12.5-B and 3Ru/BEA12.5-B samples

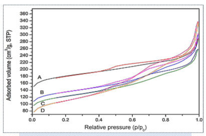


DRIFT spectra of BEA18.5, 1Ru/BEA18.5-B, 2Ru/BEA18.5-B and 3Ru/BEA18.5-B samples

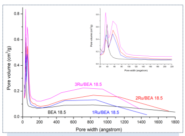
Adsorption-desorption isotherms of liquid nitrogen at -196℃:



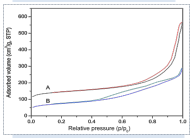
Adsorbtion-desorption isotherm of liquid nitrogen at -196°C of BEA12.5 (A), BEA18.5 (B) and BEA150 (C) samples



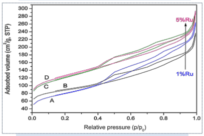
Adsorbtion-desorption isotherm of liquid nitrogen at -196°C of BEA18.5 (A), 1Ru/BEA18.5-B (B), 2Ru/BEA18.5-B (C) and 3Ru/BEA18.5-B (D) samples



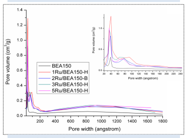
Pore size distribution of BEA18.5 (A), 1Ru/BEA18.5-B (B), 2Ru/BEA18.5-B (C) and 3Ru/BEA18.5-B (D) samples



Adsorbtion-desorption isotherm of liquid nitrogen at -196°C of BEA12.5 (A), and 3Ru/BEA12.5-B (B) samples



Adsorbtion-desorption isotherm of liquid nitrogen at -196°C of 1Ru/BEA150-H (A), 2Ru/BEA150-B (B), 3Ru/BEA150-H (C) and 5Ru/BEA150-H (D) samples



Pore size distribution of BEA150, 1Ru/BEA150-H (A), 2Ru/BEA150-B (B), 3Ru/BEA150-H (C) and 5Ru/BEA150-H (D) samples

Conclusions

✓All the characterizations confirm the successfully preparation of 10 bifunctional Ru-based catalysts, by using beta zeolite (Si/Al=12.5, 18.5 and 150), as carriers and $RuCl_3xH_2O$ as precursor for supported ruthenium particles.

✓The characterization indicates the formation of hierarchically porous structure with micro-, mezo- and macropores.

✓Different kinds of ruthenium species were noticed in the obtained samples, such as RuO_2 particles and Ru metal crystallites.

✓Catalysts will be applied in the hydrogenation of levulinic acid and succinic acid.

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Poster # 4

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Materials from biomass
Summer School
September 12-16, 2022

BIOMASS VALORIZATION BY ENZYMATIC GRAFTING OF LIGNIN

Sabina Gabriela ION [a*], Bogdan COJOCARU[a], Vasile I. PÂRVULESCU[a] *and* Mădălina TUDORACHE [a]
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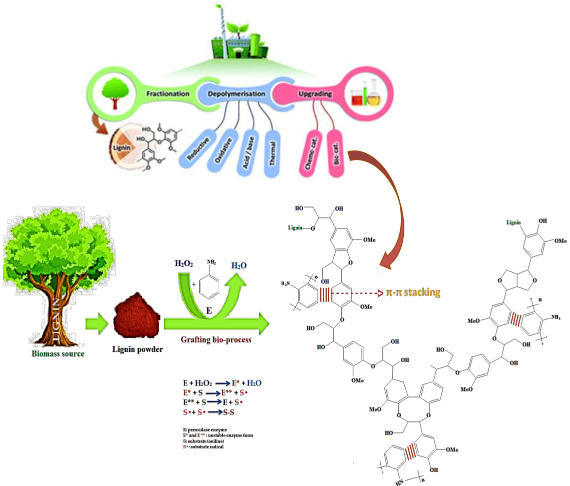


Grafting oxi-copolymerization process.

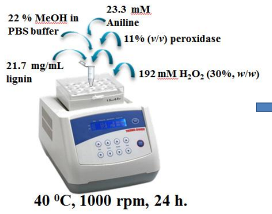
Introduction

Lignin is a heterogeneous 3D polymer which contains phenylpropane units with characteric side chains. Its structure is the effect of the strong intra/inter-molecular hydrogen interactions generated by the multiple functional groups that make difficult the change of the properties. Thus, the hydroxyl group of lignin plays a crucial role. By chemical and thermal decomposition, a wide range of chemicals can be obtained from lignin that can be used as starting materials for synthetic polymers (polyesters, polyethers and polystyrene derivatives). On the other hand, a variety of polymers can be derived from lignin by chemical/biochemical modification [1]. However, the treatment of lignin with key enzymes may afford new polymers with predictable characteristics [2]. Based on this, we focused our research on the identification of new biocatalytic routes for the addition of new functional groups able to afford a structural control.

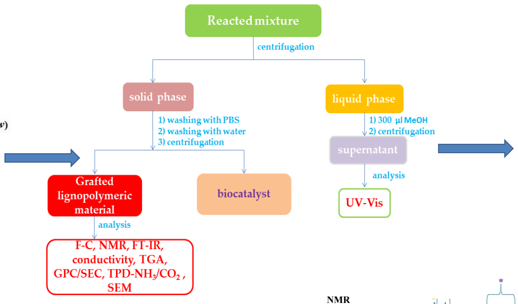
This study presents a biocatalytic alternative for the derivatization of lignin based on a grafting approach (grafting bioprocess) using aniline as the co-monomer. The insertion of aniline in the lignin structure was performed using peroxidase enzyme as the catalyst and H_2O_2 as the oxidation reagent. The monitoring of the enzymatic process was carried out based on UV-Vis and Folin-Ciocalteu (F-C) analyses. FTIR and NMR techniques allowed identifying the presence of the amine groups in the grafted lignin. Additionally, the grafted lignopolymeric material was characterized by performing gel permeation chromatography (GPC), thermogravimetric analysis (TGA) and conductivity, temperature-programmed desorption (TPD-NH_3/CO_2) and scanning electron microscopy (SEM) analyses [3]. Therefore, the reported study offers a detailed overview on biografting lignin with aniline following two aspects: (i) the performance of the enzymatic process under different experimental conditions and (ii) the characteristics of the grafted lignin related to the original lignin.

Results

➢ Evaluation of grafting bio-process

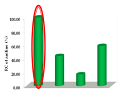


40 ^{0}C, 1000 rpm, 24 h.

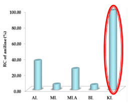


Reacted mixture
centrifugation
solid phase
1) washing with PBS
2) washing with water
3) centrifugation
Grafted lignopolymeric material
analysis
F-C, NMR, FT-IR, conductivity, TGA, GPC/SEC, TPD-NH_3/CO_2 , SEM
biocatalyst
liquid phase
1) 300 µl MeOH
2) centrifugation
supernatant
analysis
UV-Vis

➢ Optimization of the biocatalytic performance

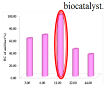


a. Enzyme screening.



b. Lignin source in the presence of the HRP biocatalyst.

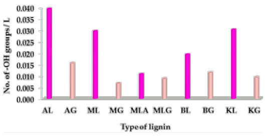
AL—alkali lignin provided by Sigma-Aldrich (St. Louis, MO, USA);
ML—*Miscanthus* lignin extracted under acidic conditions;
MLA—*Miscanthus* lignin extracted under alkali conditions;
BL—beech lignin extracted by acid-H_2O_2 treatment;
KL—lignin extracted using the Klason approach).



HRP exhibited the highest catalytic capacity of aniline insertion (100 % RC).

c. The effect of the HRP concentration on the grafting bio-process.

➢ Characterization of the ligno-polymers

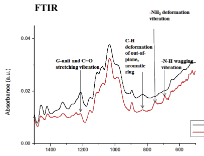


Experimental conditions: 21.70 mg/mL lignin, 23.30 mM aniline, 192 mM H_2O_2 (30%, *w/w*), 11% (*v/v*) peroxidase enzyme (2.5 U mg^{-1} peroxidase activity) and 22% MeOH in PBS (10 mM, pH 7.4); 24 h, 40 °C and 1000× *g* rpm, UV-Vis, 280 nm.

Experimental conditions for Folin-Ciocalteu approach: 10 mg/mL polymer in MeOH, 20 µL solution, 1,54 mL distilled water, 100 µL Folin-Ciocalteu reagent, 300 µL saturated solution of Na2CO3, stirring, 2h in the dark, λ=765 nm, calibration curve 0-0.5 M Coniferyl alcohol.

Differences between original (AL, ML, MLA, BL, KL) and grafted polymers (AG, MG, MLG, BG, KG) related to the free –OH groups.

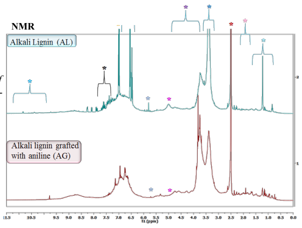
FTIR



FT-IR spectra of Klason lignin (KL) and its grafted polymer (KG).

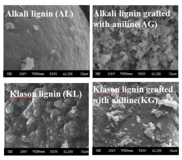
Confirmation of the grafting bio-process.

NMR

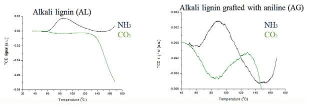


*Carboxyl and aldehyde groups
*Aromatic protons in hydroxy-phenyl units(H)
*Aromatic protons in guaiacyl units(G)
*Aromatic protons in syringyl units(S)
*Aromatic protons in polyaniline/copolymers lignin-aniline (only in derivatised lignin)
* H_α in β-5' structures
* NH protons from polyaniline (only in derivatised lignin)
* H_α and H_β in β-O-4 structures and H_γ in β-β' structures
* Methoxyl protons
* DMSO-d_6
* Aliphatic acetate protons
* Aliphatic protons

Morphology (SEM images)



Acidity/basicity analysis (NH_3/CO_2 TPD)

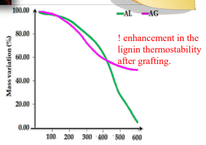


Sample	Basicity (µmol/g)	Acidity (µmol/g)
Alkali lignin (AL)	5.8	10.9
Alkali lignin grafted with aniline (AG)	16.9	4.5

Experimental conditions: the sample was heated to 120 °C with 5 °C min^{-1} for 30 min, in 30 mL highly pure helium flow in order to remove all the impurities. Then, it was cooled down to room temperature in helium flow. The adsorption of NH_3/CO_2 was carried out under ambient conditions for 1 h in a flow of 10% NH_3/CO_2 in helium (30 mL min^{-1}). For NH_3/CO_2 desorption, the sample was heated up to 170 °C at a heating rate of 5 °C min^{-1}.

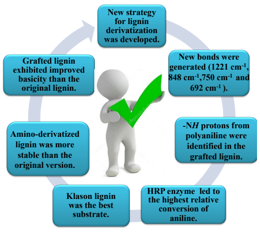
Thermostability

Thermogravimetric analysis (TGA) profiles of AL and AG; 36 °C - 600 °C in nitrogen atmosphere.



! enhancement in the lignin thermostability after grafting.

Conclusions



New strategy for lignin derivatization was developed.
New bonds were generated (1221 cm^{-1}, 848 cm^{-1},750 cm^{-1} and 692 cm^{-1}).
-*NH* protons from polyaniline were identified in the grafted lignin.
HRP enzyme led to the highest relative conversion of aniline.
Klason lignin was the best substrate.
Amino-derivatized lignin was more stable than the original version.
Grafted lignin exhibited improved basicity than the original lignin.

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Poster # 5

BioMat
11-17th September 2022

A circular economy concept: from biomass wastes to CQD/TiO_2 catalysts with enhanced photodegradation efficiency of organic dyes

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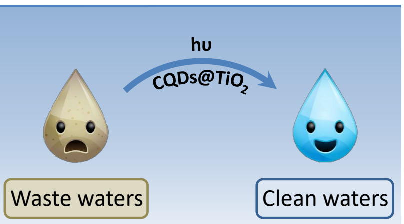
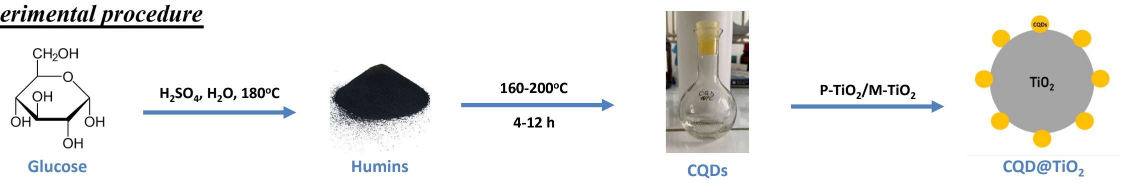
Introduction

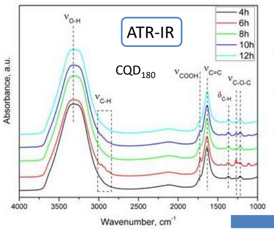
Photocatalytic reactions driven by sunlight represent a promising way to address the increasing environmental and energy concerns. To date, various photocatalytic semiconductors were used to improve the visible light assisted reactions. However, by far, titanium dioxide (TiO_2) is the most studied due to its abundance, low cost, low toxicity, great photostability, and high intrinsic catalytic activity under UV irradiation [1]. Nevertheless, the poor responses to visible light caused by its wide bandgap (3.0–3.2 eV) and the fast recombination of photogenerated electron-hole pairs limit its application in photocatalysis [2]. As to improve the photocatalytic properties of the TiO_2 a combination with carbon structures was investigated. Particularly, Carbon Quantum Dots (CQDs) were used to address the problem of the wide bandgap. The induced modifications are controlled by the CQDs dimensions [3]. Here we present the development of CQD@TiO_2 nanocomposites with potential photocatalytic activity in the purification of waste waters. For testing the activity of the new material, methylene blue (MB), an example of dyestuff resistant to biodegradation, was used.

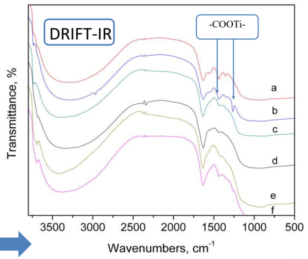


Experimental procedure

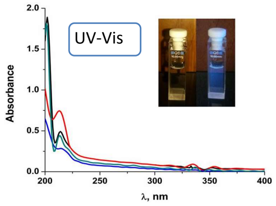


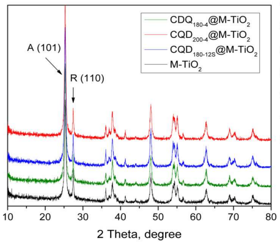
Characterizations

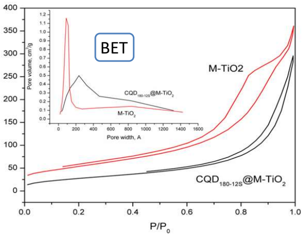


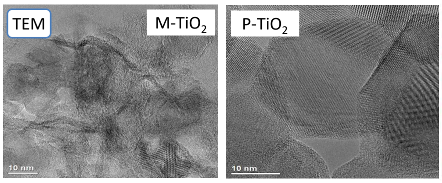


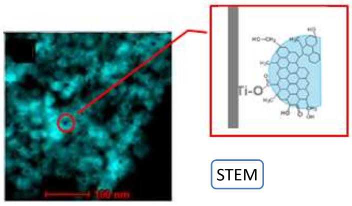
Sample	S_{BET} (m^2/g)	Pore volume (cm^3)
P-TiO_2	54	0,31
M-TiO_2	194	0,56
$CQD_{180-12S}$@M-TiO_2	203	0,45



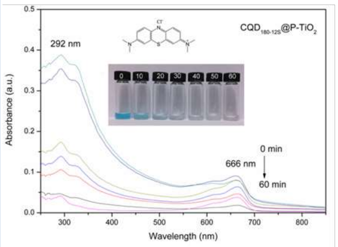


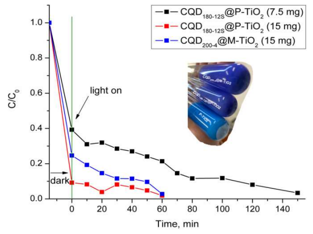


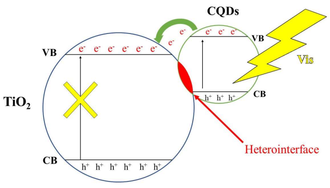




Catalytic results







Conclusions

New photocatalytic composites for the MB dye degradation were successfully synthesized. CQDs act as photosensitizers to narrow the bandgap of TiO_2 and enlarge the absorption range capability of TiO_2 into the visible light region. CQDs act as electron donors, transferring photo-generated electrons to the VB of TiO_2 providing more electrons for the degradation process and enhancing the separation of photo-generated electron–hole pairs. The heterointerface also contributes to their separation.

References

[1] Liu, J., Zhu, W., Yu, S., Yan, X., Carbon, 79 (2014) 369-379. **[2]** Ohno, T., Sarukawa, K., Tokieda, K., Matsumura, M., J Catal., 203 (2001) 82-86. **[3]** Wang, X., Cao, L., Lu, F. S., Meziani, M. J., Li, H. T., Qi, G., Zhou, B., Harruff, B. A., Kermarrec, F., Sun, Y. P., Chem. Commun., (2009) 3774-3776.

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Poster # 6

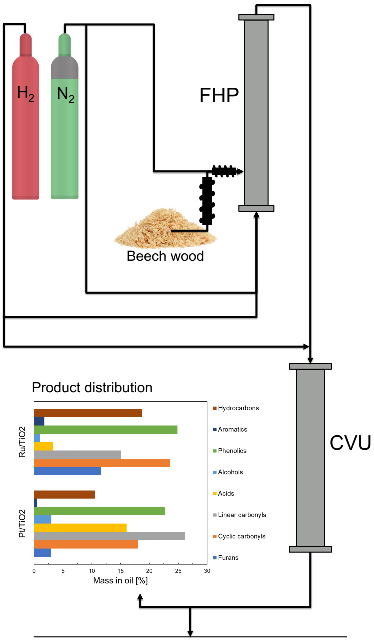
Beech wood bio-oil catalytic upgrading at laboratory pilot plant scale: evaluation of the biofuel and carbon deposits

Albert Miró i Rovira, Felix Herold, Petter Tingelstad,
Kumar R. Rout, De Chen

1. Introduction Bio-oil, by means of fast hydro-pyrolysis (FHP), is a promising renewable intermediate to produce liquid fuels. However, FHP bio-oil contains a high percentage of reactive oxygenated compounds, therefore, it is necessary to upgrade the bio-oil by means of catalytic vapor upgrading (CVU). Nevertheless, CVU processes suffer from the formation of coke (both thermal lignin and aromatic coke by polymerization of unstable bio-oil compounds) which leads to severe catalyst deactivation.

To attenuate the coke formation a two-step catalytic HDO has been proposed. An initial first step is carried out to partially remove reactive oxygenates under mild conditions in order to reduce the coke formation in the second step. For this initial bio-oil stabilization stage, it has been proposed that the utilization of a bifunctional catalyst exhibiting redox as well as acid centers, which prevents high formation rates of coke compared to catalysts that have been generally used in biomass conversion.

2. Pilot plant Catalytic upgrading experiments from beech wood were performed in a mini-pilot plant set-up, with a fluidized bed reactor, for the FHP (500° C), and a fixed bed reactor for the catalytic vapor upgrading (350° C). Two upgrading catalysts, 1wt% Ru/TiO_2, and 1wt% Pt/TiO_2 were tested.

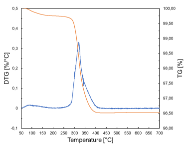


Catalyst	Solid [%]	Liquid (Aqueous + oil) [%]	Gas [%]
Ru/TiO_2	19,00	13,62 + 15,06	22,50
Pt/TiO_2	19,75	13,33 + 14,62	34,33

3. Coke analysis For the characterization of the carbon deposits formed over the catalysts used for CVU, Thermogravimetric Analysis (TGA), Raman spectroscopy, and X-Ray Photoelectron Spectroscopy (XPS), have been utilized. The obtained results are summarized in the following figures:

1wt%-Ru/TiO_2

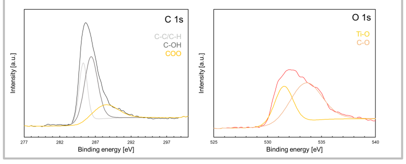
TGA:



Raman:

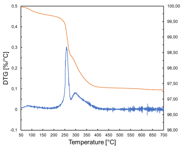
Run	I_D/I_G	Shift G	HWHM G
Spectrum 1	1,00	1596,0	44,6
Spectrum 2	1,00	1602,1	48,7
Spectrum 3	0,97	1595,4	52,1
Average	0,99 ± 0,02	1597,8 ± 3,0	48,5 ± 3,0

XPS:



1wt%-Pt/TiO_2

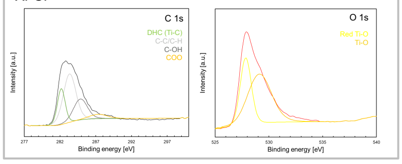
TGA:



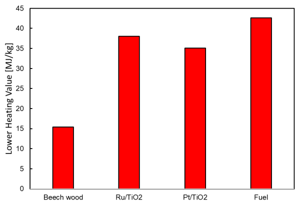
Raman:

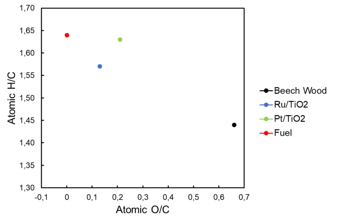
Run	I_D/I_G	Shift G	HWHM G
Spectrum 1	0,94	1599,6	41,6
Spectrum 2	0,97	1595,7	39,8
Spectrum 3	0,92	1596,7	39,3
Average	0,94 ± 0,02	1597,2 ± 1,7	40,1 ± 0,8

XPS:



4. Fuel analysis For the characterization of the properties of the upgraded bio-oil (biofuel) the Van-Krevelen diagram, and the lower heating values of the oils obtained with the developed catalysts are reported and compared to beech wood (feedstock) and convectional diesel fuel (target).





5. Conclusion Both catalyst are able to upgrade the beech wood pyrolysis oil, converting it to a biofuel with similar properties to conventional diesel fuel. However, the Ruthenium-based oil has a higher heating value, a lower O/C ratio, and lesser presence of organic acids than the Platinum based catalyst, which improves the biofuel stability.

The coke formation on both catalysts is similar in both, the amount of carbon accumulated and its structure, which consists of nanocrystalline structures that do not form an ordered material. However, in the Pt based catalyst, through XPS analysis, it is observed that the carbon is bonding with the support forming TiC on the surface.

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