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BOOK OF ABSTRACTS

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Catalysis and chemical engineering as enabling elements for circular economy

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Ways to a circular economy: current status and initiatives

Dr. Enrico Barsch, Projektträgerschaft Ressourcen, Kreislaufwirtschaft, Geoforschung, Forschungszentrum Jülich GmbH, Germany

The European Green Deal is EU's path to a sustainable economy. It provides an action plan to boost the efficient use of resources by moving to a clean, circular economy. To reach climate goals it will be essential to establish a circular carbon economy. Fossil resources need to be replaced by sustainable carbon sources. Improved recycling, biomass and the use of CO2 will demand new processes, especially in the chemical industry. Research and innovation is a prerequisite for a successful transformation and catalysis will be one of the most important elements in this process. Germany has excellent opportunities but will need to intensify its efforts to become a leading player in the transformation towards sustainability.

The German Federal Ministry of Education and Research (BMBF) recently published the new FONA strategy. It which provides a framework and describes several actions to support research for sustainability. With a focus on circular carbon economy the talk will give a brief overview on BMBF research programs and funding options for catalysis research.

Propelling a Sustainable Catalyst Cycle

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Steve MAYO, Eurecat US, Pasadena, United States,

Catalysis in general already plays a key role for sutainable development, by limiting the environmental impacts of chemical processes. Today, in the development of clean processes, and for targeting both more responsible consumption and people and environment preservation, it is mandatory to consider new ways to use, to reuse or to recycle catalysts.

Eurecat is the interface between catalysts manufacturers, end users, and recyclers. In this position, Eurecat, together with its partners, can contribute at various levels in the catalyst cycle to support them towards a more sustainable growth.

A catalyst life cycle obviously covers manufacturing and use, but also intermediate operations as loading/unloading, restoration of the performances of the spent catalyst when possible (e.g. regeneration and optionally rejuvenation), or valorization of raw materials for further uses (see Figure 1).

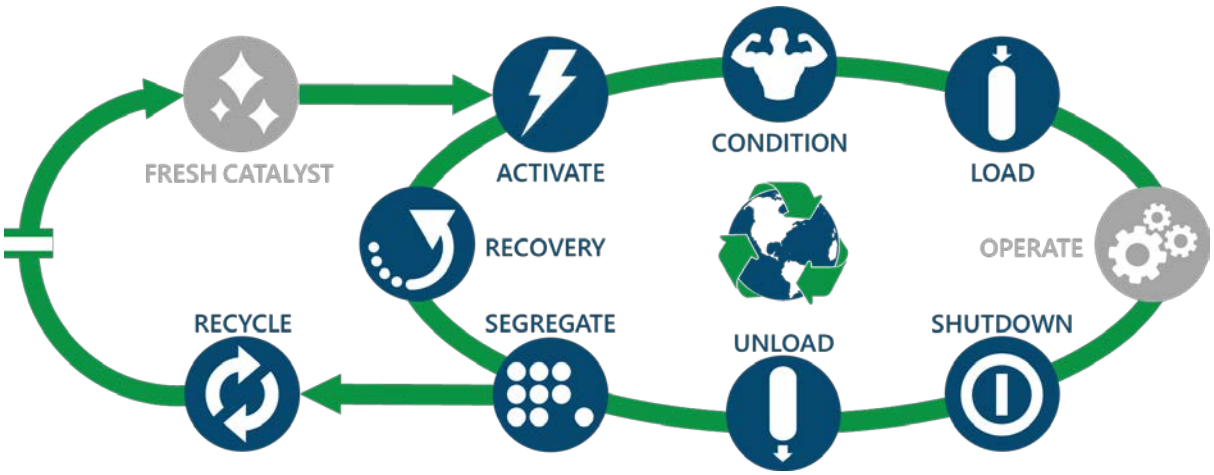

Figure 1. Example of Catalyst Cycle

Object of this presentation if to show how Eurecat has developed know-hows and innovative tools for maximizing catalysts reuse, in similar duty or for other applications, and for optimizing recycling of the raw materials. In addition, new services for a more reponsible use of catalysts, to preserve health and environment, will also be presented.

ChemCycling™ – Challenges and Opportunities of the Chemical Recycling of Plastic Waste

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ChemCycling™ is BASF´s Recycling Option for Post-Consumer Plastic Waste

BASF is strongly committed to sustainability, based on our commitment, customer requestsand regulatory obligations to increase the share of recycled materials, which all demand for innovative approaches beyond mechanical recycling. BASF has taken up this challenge with an interdisciplinary team in its ChemCycling™ project. The aim is to manufacture high-performance products from chemically recycled plastic waste on an industrial scale. BASF cooperates with technology partners who use a thermochemical process called pyrolysis to break down the plastic polymers into smaller molecules suitable for re-integration into the BASF's production network (Verbund). The share of recycled material is allocated to products manufactured in the Verbund by using a third-party audited mass balance approach. These products have the same properties as those manufactured from fossil feedstock.

Chemical recycling can contribute to increase the amount of plastic waste recycled as it can cope with waste streams for which no other high-value recycling is available or capacities are missing. An example are inhomogeneous mixed plastic waste streams. Moreover, the amount of fossil resources required for chemical production are reduced. A life cycle analysis performed by Sphera for BASF shows that pyrolysis of mixed plastic waste has the prospects of lowering carbon dioxide emissions compared to incineration by 50% [1].

Paving the Technical Path for ChemCycling™

While large volumes of sorted single-stream plastics can and should be recycled mechanically, chemical recycling can process waste streams for which it may be impossible or very inefficient to sort them for a high-value mechanical recycling. An overview of the waste fractions is shown in [2] and its implication on ChemCycling™ will be discussed. Pyrolysis in this context is a core technology as a first process step to generate pyrolysis oil which can be used as a secondary raw material in BASF's Verbund production. Challenges for the integration of the pyrolysis oil lie in the removal of undesired heteroatoms such as sulphur, oxygen or nitrogen and the simultaneous recovery of valuable products [3]. Catalysis and chemical engineering

both play a pivotal role in the generation of a feedstock suitable for the Verbund. BASF is supporting its technology partners in further developing their chemical recycling processes.

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Who needs Oil? The refinery of the future

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Summary

Oil refining produces transportation fuels and important chemical intermediates. Over the next decades, the energy transition will result in a gradual shift away from fossil raw materials. In addition, changes in the required products will drive changes in the combination of processes required. Vehicle electrification will remove the demand for gasoline, and high-energy density hydrocarbon fuels will only be required for long-distance heavy-duty transportation, and (parts of) aviation and marine transportation. At the same time, the ratio between fuels and chemical intermediates will change drastically. Finally, while new oil refineries are still being built elsewhere to accommodate medium term hydrocarbon fuel demands, European refineries are closing or transforming capacity to the conversion of e.g., biomass. What would a new European refinery in 2050 look like, and how can the combination of catalysis and process engineering contribute to these new developments? Could CO_2 be a source of carbon for hydrocarbon fuels? Could we make chemical intermediates and monomers from biomass and plastic waste? What infrastructure would be required? Could we develop the required processes at the right scale in time for a carbon neutral society in 2050?

Opportunities and challenges for catalysis in plastics upcycling

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Deposition of non-industrial plastics has emerged as one of the critical problems on a worldwide scale, leading to a substantial and currently uncontrolled imission of polymer particles in a wide dispersion of size into land and aqueous environment. Once the critical collection and basic cleaning of plastic waste is solved, the key challenge for the chemical conversion of plastics is to overcome the energy required to deconstruct the polymers and to convert the intermediates to chemical or fuel components. Balancing this energy requires a kinetic link to an exothermic reaction, including hydrogenation, ring closure reactions. Using polyolefins, as example first the main options and current progress in cleaving C-C bonds will be compared, i.e., the metal catalyzed hydrogenolysis and metathesis and the acid catalyzed protolytic cleavage. The currently most successful catalysts for hydrogenolysis and metathesis are based on noble metals; finding abundant base metals for this chemistry will be critical for a wide acceptance. The difficulty with acid catalysts, in contrast, is related to high activation energies and the need to use relatively high temperatures. Finally, the cross sensitivity for conversion of polymer mixtures will be discussed.

Enhanced CO_2 methanation activity over $La_{2-x}Ce_xNiO_4$ perovskite-type catalysts: understanding the structure-performance relationships

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Hydrogenation of CO_2 to methane is considered as one of the most important strategic reactions to produce value-added chemicals and for storage of renewable energy (power-to-gas) [1]. At this point, an excellent catalyst and especially a clear understanding of structure-activity relationships in CO_2 methanation are the key steps for the commercial feasibility of the process [2]. Recently, our group synthesized $La_{2-x}Ce_xNiO_4$ perovskite-type catalysts by a sol-gel method, and various characterization techniques (e.g., H_2-TPR, HRTEM, Qusi in-situ XPS, In-situ DRIFTS) were employed to carefully elaborate structure-performance relationships in CO_2 methanation [3]. Based on careful characterization and experimental results of CO_2 methanation over $La_{2-x}Ce_xNiO_4$ catalysts, $La_{2-x}Ce_xNiO_4$ with a La/Ce ratio of 0.5/1.5 ($La_{0.5}Ce_{1.5}NiO_4$) and 11 wt.% Ni was found to be the most active catalyst under experimental conditions, which exhibited the highest CO_2 conversion rate of 57.4 $mmolCO_2/mol_{Ni}/s$ and 99.8% CH_4 selectivity at 350 °C (**Figure 1a**).

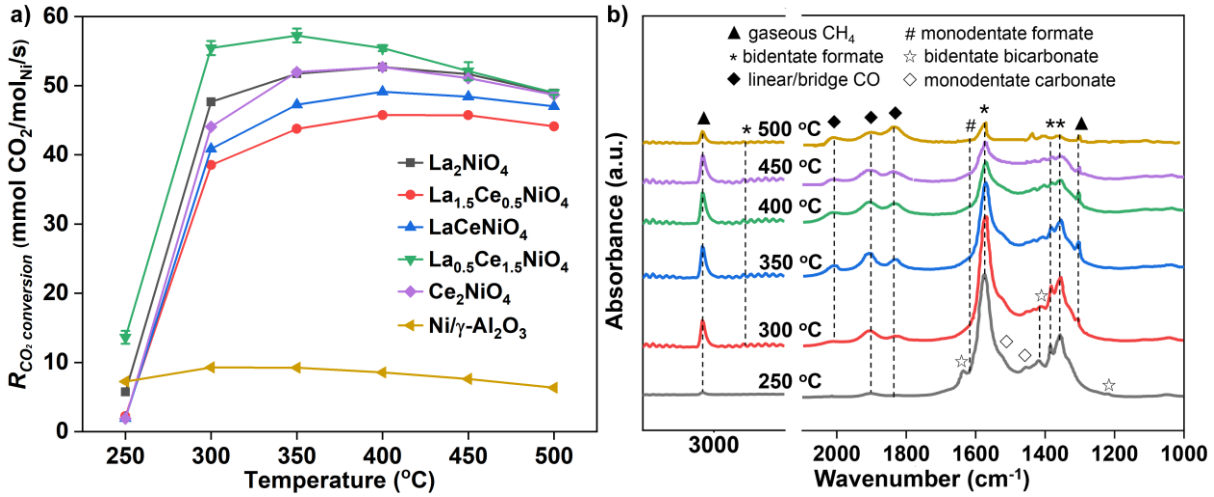

Figure 1. CO_2 conversion rate over $La_{0.5}Ce_{1.5}NiO_4$ (a) at different temperatures and (b) under different steam concentrations.

To understand the mechanism of $La_{0.5}Ce_{1.5}NiO_4$ and commercial Ni/γ–Al_2O_3 catalyst in CO_2 methanation, we carried out in-situ DRIFTS experiments under simulated mixtures. The results revealed that CO_2 methanation over the prepared $La_{0.5}Ce_{1.5}NiO_4$ and commercial Ni/γ–Al_2O_3 followed the CO route and formate route, respectively. According to the results of quasi in-situ XPS, CO_2-TPD, and HR-TEM for all synthesized $La_{2-x}Ce_xNiO_4$ catalysts, $La_{0.5}Ce_{1.5}NiO_4$ possessed a higher content of oxygen vacancies (25.3%), a favorable content of weak and medium basic sites, smaller Ni particle size (10.2 nm) and bigger Ni (111) plane than others (**Figure 2a**). Based on the characterized results, we considered tailored basicity, reducibility, oxygen vacancies, Ni dispersion, and exposed Ni (111) crystal plane beneficial for efficient methane production. The possible pathways for methane production over $La_{0.5}Ce_{1.5}NiO_4$ and commercial Ni/γ–Al_2O_3 are summarized in **Figure 2b**.

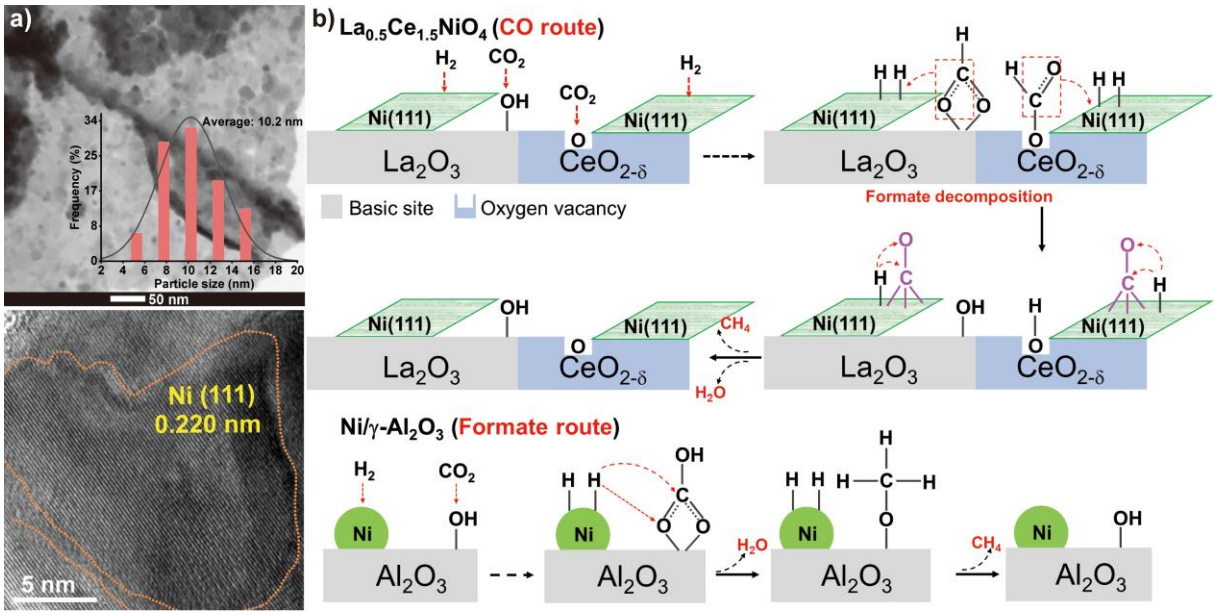

Figure 2. (a) In-situ DRIFT spectra of $La_{0.5}Ce_{1.5}NiO_4$ under mixtures at 250-500 °C and (b) Possible methanation pathways over $La_{2-x}Ce_xNiO_4$ catalyst and commerical Ni/γ–Al_2O_3 catalyst.

In addition, $La_{0.5}Ce_{1.5}NiO_4$ catalyst exhibited a stable performance during 100 h time of stream testing, and the catalyst can endure dynamic mixtures feeding with different H_2/CO_2 ratios. Importantly, activity loss of $La_{0.5}Ce_{1.5}NiO_4$ when treated by 10%-50% steam can be recovered by reduction.

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Depolymerization of Technical Grade Polyamide 66 and Polyurethane Materials via Hydrogenation

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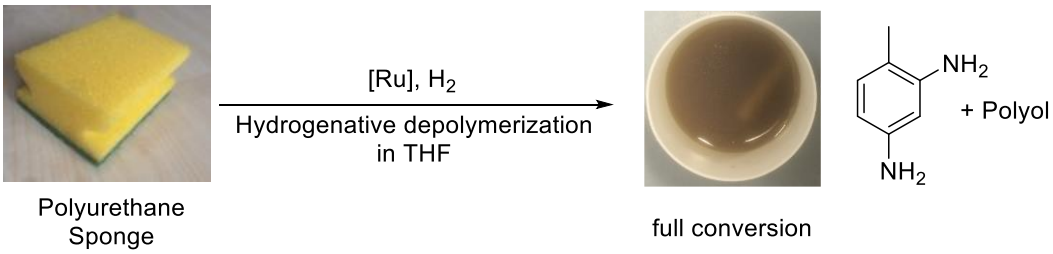
The widespread and increasing use of plastics poses a great challenge for the sustainability of human society. Until now, the majority of these post-consumer polymers are discarded, being either landfilled, incinerated or illegally dumped in the oceans.[1] Thus, it is crucial to establish efficient recycling process to avoid the pollution with plastic waste and also to save fossil feedstocks in the monomer synthesis. In this regard chemical recycling is a promising approach since the process leads to the desired monomers. Hereby the hydrogenative depolymerization of polyamide 66 and polyurethane using a Ru-pincer complex is presented.[2]



Scheme 1. Hydrogenative depolymerization of a kitchen sponge using Ru-catalyst

The system features high reaction temperature and hydrogen pressure with THF as solvent. Substantial amount of products were achieved when even technical grade polymers were applied. The procedure can also be applied on a lager scale (10g of PU foam was successfully depolymerized applying only 0.02 mmol of Ru catalyst). Remarkably, turnover number close to 1000 is obtained for the hydrogenation of a household kitchen sponge.

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Efficient Photocatalytic Oxidation of Aromatic Alcohols over Thiophene-based Covalent Triazine Frameworks with A Narrow Band Gap

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Photocatalytic selective oxidation of aromatic alcohols by covalent organic frameworks (COFs) is a sustainable strategy to replace present metal-based heterogeneous catalytic oxidation systems. Covalent triazine-based frameworks (CTFs), a subgroup of COFs, possess promising properties as efficient catalysts for photocatalytic oxidation. Sulfur-containing metal-free CTFs exhibit a good performance in photocatalysis due to their narrowed band gap, and the fast generated photoelectrons/holes separation and transfer. Here, we report the synthesis of thiophene-based CTFs under mild conditions for photocatalytic oxidation of aromatic alcohols to the corresponding benzaldehydes using pure oxygen as the oxidant. Full conversion and a selectivity as high as 90% to benzaldehyde were obtained paving the way for a potential application of these metal-free photocatalysts in fine chemicals synthesis.

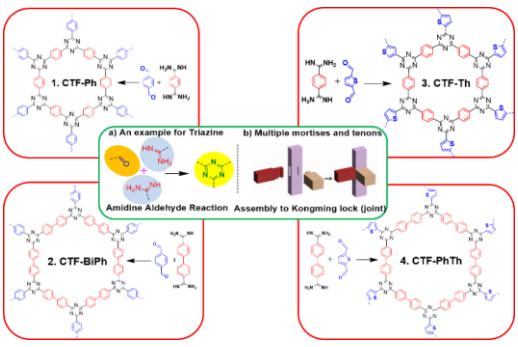

Figure 1. Illustrated formation of thiophene-based CTFs (CTF-Th, CTF-PhTh) and phenyl-based CTFs (CTF-Ph, CTF-BiPh). (a) Amidine-aldehyde formation of triazine. (b) Ancient synthetic scaffolds combining multiple mortises and tenons.[1]

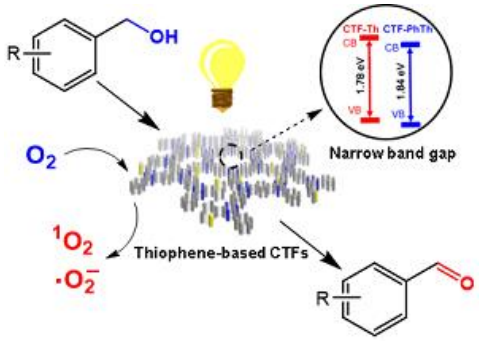

Figure 2. Illustrated photocatalytic oxidation of aromatic alcohols into the corresponding benzaldehydes over thiophene-based CTFs.

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Dimethoxymethane synthesis by the gas-phase nonoxidative dehydrogenation of methanol over Cu/H-BEA bifunctional catalysts

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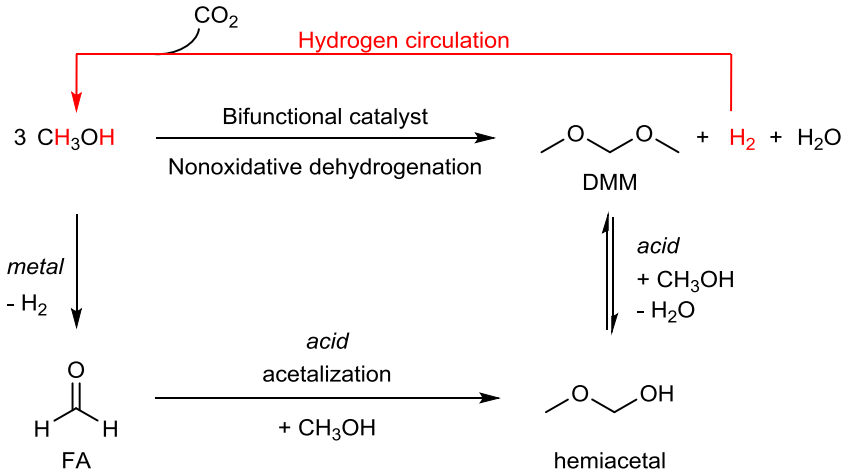
Transportation is one of the main sectors contributing to global greenhouse gas emissions. Therefore, considerable effort is still required for sustainable mobility. Recently, synthetic fuels based on CO_2 and H_2 are considered promising for the reduction of CO_2 emissions by CO_2 consumption during fuel production. Such processes enable to substitute fossil fuels by renewable feedstock. Moreover, the substitute fuel can be also directly used as a drop-in fuel without major modifications to the existing transportation system. Various CO_2-based compounds such as oxymethylene ethers (OME) have been suggested as potential diesel fuel additives. OMEs with medium chain length have attracted attention, owing to their excellent ability in reducing soot formation and good compatibility with diesel engines. Among the OMEs, dimethoxymethane (DMM) is the simplest compound and its current production relies on an oxidative reaction route with the formation of H_2O leading to low H_2 efficiency. Therefore, recently, our group presented a novel gas-phase DMM synthesis strategy (**Scheme 1**) via the nonoxidative methanol dehydrogenation with the formation of H_2 instead of H_2O [1 - 3]. This approach appears to be highly attractive due to the potential closed H_2 circulation, thus improving the overall energy efficiency of the process.



Scheme 1. DMM synthesis by gas-phase nonoxidative dehydrogenation of methanol.

For selective DMM synthesis via dehydrogenation of methanol, a suitable bifunctional catalyst with both acidic and dehydrogenation sites is necessary. Hence, herein we report Cu/H-BEA as potential bifunctional catalysts. Among the prepared catalysts, the sample with higher Si/Al ratio (Si/Al = 836) presented the highest activity and selectivity towards DMM. 81.5% selectivity was achieved with a methanol conversion of 3.7% at 1 atm and 200°C. Interestingly, an induction period featuring a remarkable rise in DMM selectivity from 41 to 81.5% with time on stream occurred. Besides, detailed characterization results indicate an adaptation of Cu species and Lewis acidic sites under reaction conditions resulting in the decisively weaker dehydrogenation and condensation ability for high DMM selectivity.

This work was funded by the German Federal Ministry of Education and Research within the project NAMOSYN: Nachhaltige Mobilität durch synthetische Kraftstoffe (03F0566P0).

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From Succinic Acid to *N*-Vinyl-2-Pyrrolidone Monomers: A Catalyst Design and Life Cycle Analysis Perspective

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Succinic acid (SA) has been identified as one of the most promising platform chemicals derivable from biomass carbohydrates.[1] The development of conversion technologies and value chains connecting SA to valuable products is thus an important part of biorefinery research.[2] Insights in this field will help to directly integrate CO_2-binding photosynthesis with chemical production, which might constitute an important link in a circular carbon economy.

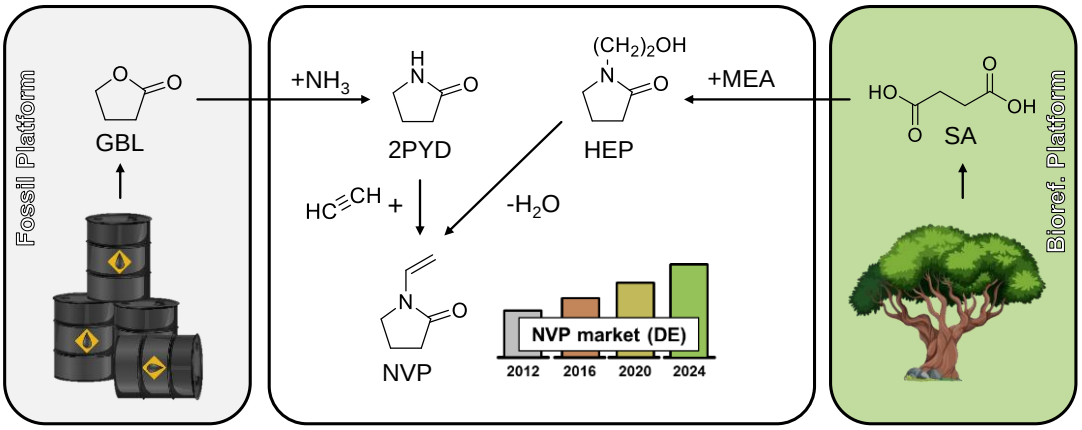

Figure 1: Bio-based and fossil alternatives to produce *N*-vinyl-2-pyrrolidone. GBL, γ-butyrolaction; 2PYD, 2-pyrrolidone; MEA, monoethanolamine, HEP, *N*-(2-hydroxyethyl)-2-pyrrolidone.[4]

In this context, we have previously proposed the two-step synthesis of *N*-vinyl-2-pyrrolidone (NVP), a high-value monomer, from succinic acid.[3] The corresponding process starts with an amidation-hydrogenation reaction, employing monoethanolamine (MEA), molecular hydrogen and a supported metal catalyst. The target intermediate, *N*-(2-hydroxyethyl)-2-pyrrolidone (HEP), is then dehydrated over basic Na_2O/SiO_2 in a gas phase reaction (**Figure** 1). SA-based NVP yields around 70 mol% were already reported. A detailed comparison with the fossil alternative may thus unveil the merits of bio-based NVP production, while defining future research priorities at the same time.

This contribution discusses a *cradle-to-gate* life cycle and cost analysis of several NVP production alternatives. It is based on rigorous Aspen® process models and the evaluation of the corresponding life cycle inventories. Next to standard scenarios for

fossil (*Fos*) and bio-based (*Bio*) production, different hydrogenation catalysts (Ru *vs.* PtRe) are considered to account for the developmental stage of SA-to-NVP conversion.

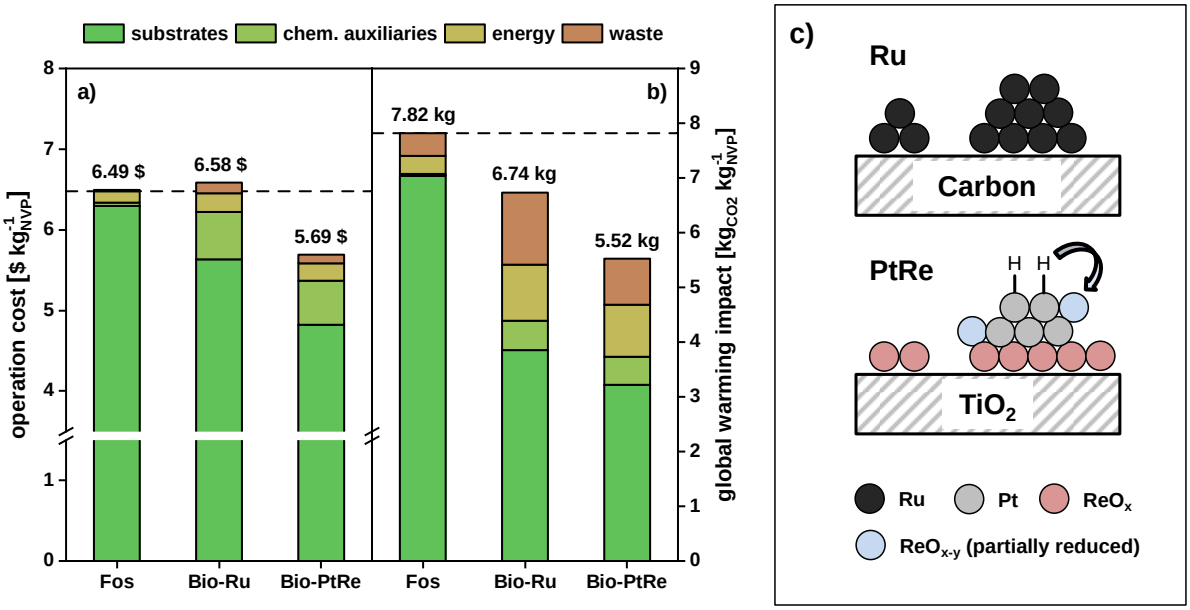

Figure 2: Analysis of alternative processes for NVP synthesis. a) operation costs, b) global warming impact and c) display of catalyst systems developed for the bio-based process.

In short, the corresponding results highlight the potential of SA-based NVP production to lower both, the cost (**Figure** 2**a**) and the economic impact (**Figure** 2**b**) associated with 1 kg of monomer. However, the economic success of the new value chain is directly dependent on a stable market for reasonably-priced SA (≤ 2.5 $ kg$_{SA}$). Moreover, an efficient amidation-hydrogenation catalyst (**Figure** 2**c**) is the most important technological prerequisite for the viability of the *Bio* route. In this context, bimetallic Pt-Re/TiO_2 outperforms the previously set Ru/C benchmark due to preferential chemoselectivity. While this leads to a 12 % (relative) reduction in operation costs, 31 % would be attainable with an idealized (S = 100 %) material. Notable potential for future development thus lies in catalyst design.

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Smart light driven micromotors as tools in microplastic recycling

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Microswimmers have attracted considerable scientific interest due to their autonomous motion on the nano/micro scale.[1,2] However, the applications in biological and environmental fields are limited by the requirement of high energy fuels that are often toxic or oxidizing. Photocatalytic microswimmers are based on photocatalytic reactions. Benefitting from light as renewable energy and 'green' fuel (water), they extend the application potential in different fields, especially in environmental remediation.

To study the basic behavior of photocatalytic microswimmers in different fuels and irradiation conditions, we used semiconductor TiO_2 colloids as base material for microswimmers. [3]

Here, we elucidate how the fuel and irradiation conditions influence the gradients around the particles which translate into motion. These conditions were probed by traditional analytics as well as using passive colloids as probes and we will give an overview of first environmental applications, owing to efficient activity, environmental friendliness, low-cost and chemical stability of the material.[4]

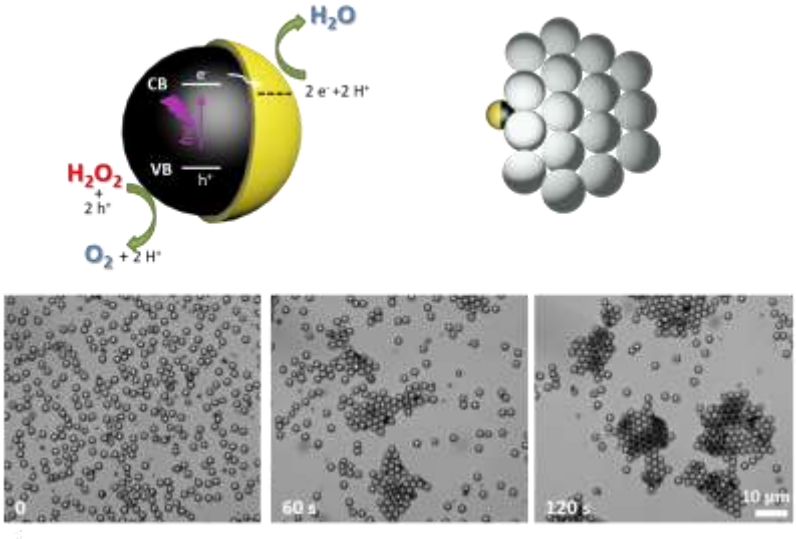

Figure: Au@TiO2 microswimmer, catalytic principle and scheme of raft formation. Micrographs showing active assembly of micro-plastics (PS spheres).

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