

Statistics

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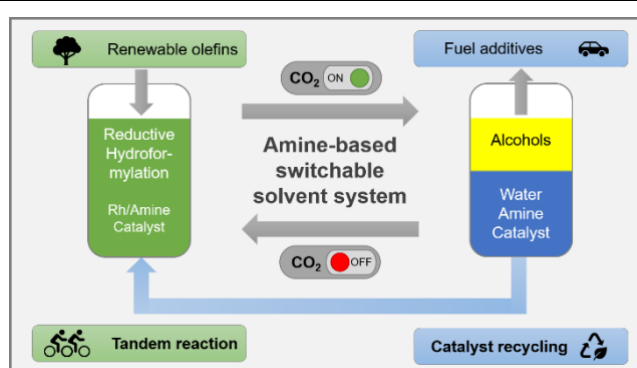
2022

<p>97. M. Schrimpf, P. A. Graefe, A. Holl, A. J. Vorholt*, W. Leitner “Effect of liquid-liquid interfacial area on biphasic catalysis exemplified on hydroformylation” <i>ACS Catalysis</i>, accepted, DOI: https://onlinelibrary.wiley.com/doi/10.1002/anie.202201004</p>	
<p>Biphasic catalysis enables effective recycling of homogeneous catalysts by their immobilization in an additional liquid phase immiscible with the products. The introduced liquid-liquid interfacial area implies mass transfer limitations that play an important role in understanding these catalytic systems, with many rate enhancement strategies revolving around optimizing said area. In this contribution, the relationship between liquid-liquid interfacial area and catalytic activity is elucidated by applying a methodology that utilizes an image-based in-situ measurement of the transient droplet size distribution. Taking the industrially highly relevant aqueous biphasic hydroformylation of the long-chain olefin 1-octene as the model reaction, it is found that the product nonanal and the addition of the ligand increases the interfacial area by a factor of up to five. The rate of conversion is found to depend on the stirring speed. By varying the catalyst concentration, it is shown that an accumulation of the catalyst species at the interface is unlikely. Using a mathematical model, it is highlighted that the effect of the aqueous/organic interfacial area on the catalytic activity is not linear as previously assumed in literature. Instead, a change in the interfacial composition is proposed that causes a shift in the dependency of catalytic activity on said area. To our knowledge, for the first time, the dynamic physical properties of a lean gas-liquid-liquid system were linked to the catalytic performance of the system.</p>	

<p>96. K. Jeske, T. Rösler, M. Belleflamme, T. Rodenas, N. Fischer, M. Claeys, W. Leitner, A. J. Vorholt, G. Prieto “Direct Conversion of Syngas to Higher Alcohols via Tandem Integration of Fischer-Tropsch Synthesis and Reductive Hydroformylation” <i>Ange Chem.</i>, accepted, DOI: 10.1002/anie.202201004</p>	
<p>The selective conversion of syngas to higher alcohols is an attractive albeit elusive route in the quest for effective production of chemicals from alternative carbon resources. We report the tandem integration of solid cobalt Fischer-Tropsch and molecular hydroformylation catalysts in a one-pot slurry-phase process. Unprecedented selectivities (>50 wt%) to C2+ alcohols are achieved at CO conversion levels >70%, alongside negligible CO₂ side-production. The efficient overall transformation is enabled by catalyst engineering, bridging gaps in operation temperature and intrinsic selectivity which have classically precluded integration of these reactions in a single conversion step. Swift capture of 1-olefin Fischer-Tropsch primary products by the molecular hydroformylation catalyst, presumably within the pores of the solid catalyst is key for high alcohol selectivity. The results underscore that controlled cooperation between solid aggregate and soluble molecular metal catalysts, which pertain to traditionally dichotomic realms of heterogeneous and homogeneous catalysis, is a promising blueprint toward selective conversion processes.</p>	

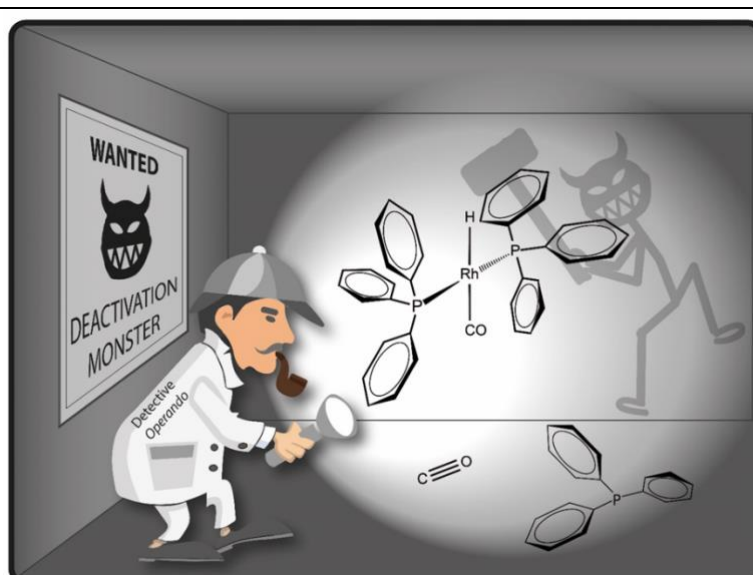
<p>95. J. Vossen, A. J. Vorholt*, W. Leitner “Catalyst Recycling in the Reactive Distillation of Primary Alcohols to Olefins using a Phosphoric Acid Catalyst”, <i>ACS Sus. Chem. & Eng.</i>, accepted, DOI: 10.1021/acssuschemeng.2c00237</p>	
<p>Olefins are essential basic chemicals in all areas of chemical industry and can be produced from alcohols by dehydration. The amount of alcohols produced from biomass sources is expected to rise in the next decades. Various heterogeneously catalyzed processes have been developed in previous works operating at high reaction temperatures of 350 °C to obtain olefins from alcohols. In this work we present the conversion of C₇ to C₁₂ α-alcohols to the corresponding olefins using phosphoric acid as a strong inorganic homogeneous acid catalyst. The reaction network was investigated using a microwave reactor. A system with a reactive distillation of the produced water and olefins was developed to shift the equilibrium of the reaction towards the olefins. Mild reaction conditions were utilized with temperatures ranging between 170 °C and 230 °C. The catalyst was recycled successfully over 12 runs in batch reactions and in semi-continuous flow experiments at 190 °C over 6 h. Up to 93% yield of olefinic products were obtained with the corresponding ether as the major side product</p>	

94. S. Püschel, J. Sadowski, T. Rösler, K. R. Ehmann, A. J. Vorholt*, W. Leitner
“Auto-tandem catalytic reductive hydroformylation in a CO₂-switchable solvent system”,
ACS Sus. Chem. & Eng.,
 10, 11, 3749–3756, DOI:
[10.1021/acssuschemeng.2c00419](https://doi.org/10.1021/acssuschemeng.2c00419)



The upgrading olefin-enriched Fischer-Tropsch cuts by the synthesis of alcohols leads to drop-in capable bio-synthetic fuels with low carbon emissions. As alternative to the conventional two-step production of long-chain alcohols, tandem-catalytic systems improve energy and resource efficiency. Herein, we present an auto-tandem catalytic system for the production of alcohols from olefin-paraffin mixtures. By utilization of a tertiary alkanolamine as ligand as well as switchable component in the solvent system, a lean reaction system capable of catalyst recycling was developed. The system was characterized in regard to the switchable solvent separation approach and reaction parameters, resulting in alcohol yields of up to 99.5% and Turnover Frequencies of up to 764 h⁻¹. By recycling the catalyst in 10 consecutive reactions, a Total Turnover Number of 2810 was achieved.

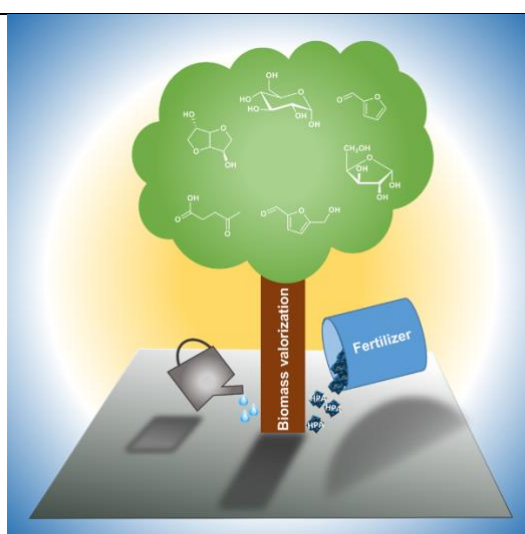
93. K. Köhnke, N. Wessel, J. Esteban, J. Jin, A. J. Vorholt*, W. Leitner
“Operando monitoring of mechanisms and deactivation of molecular catalysts”,
Green Chem.,
 2022, 24, 1951 - 1972, DOI:
[10.1039/D1GC04383H](https://doi.org/10.1039/D1GC04383H)



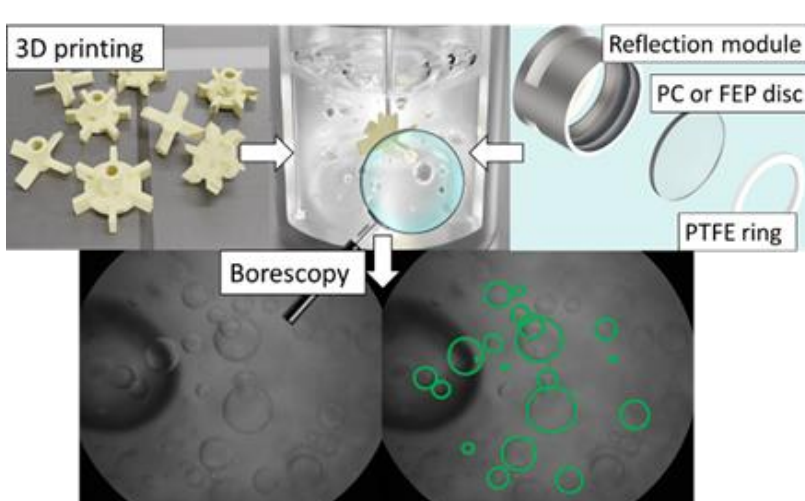
Observing and understanding the phenomena associated with the reaction mechanisms and catalyst deactivation in molecular catalysis is a very challenging task in green chemistry. This knowledge is crucial for applying and scaling catalyzed reactions as well as preventing misproduction at a very early point. Over the years, experimental arrangements have evolved towards analysis of catalysts and reaction products in the so-called *operando* setups. This contribution reflects on the potential of *operando* studies to elucidate reaction and deactivation mechanisms in homogeneous catalysis as well as the outstanding opportunities that arise from the application of *operando* experimental setups. Such setups mostly rely on spectroscopic analysis, optionally coupled with chromatographic techniques that monitor the reaction system. This in turn means that not only the evolution of the reaction substrates and products can be monitored, but also changes of the molecular catalyst species that may affect the catalytic performance. Therefore, this review focusses on techniques to monitor the catalyst under real conditions.

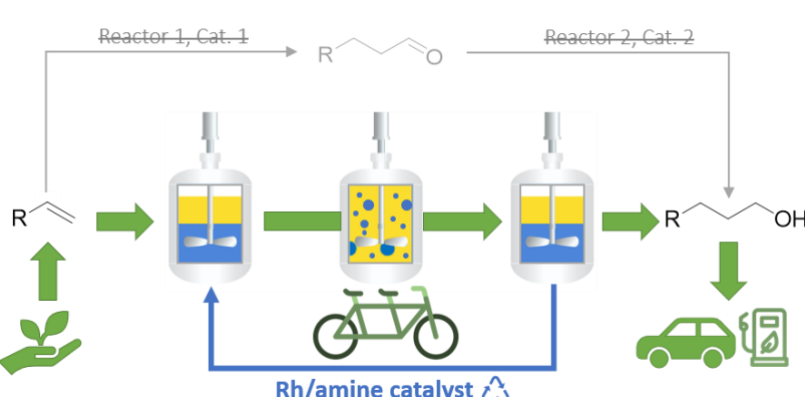
In this review, different spectroscopic techniques relevant for monitoring molecular transition metal catalysts in solution are covered, followed by numerical methods used in the chemometrics literature to undertake the challenge of untangling the complex raw signals and allocating them to individual chemical species. Finally, two exemplary case studies of industrially relevant chemical reactions are presented, namely the hydroformylation and the asymmetric hydrogenation. These examples illustrate the significance of the application of both the experimental setups as well as data processing and signal resolution to have an insight into the deactivation of catalytic systems. The *operando* approach shows high potential for the increased use in future research to develop stable and more selective catalysts which can be applied in greener processes.

92. L. Hombach, N. Simitsis, J. T. Vossen, A. J. Vorholt, A. K. Beine
“Solidified and Immobilized Heteropolyacids for the Valorization of Lignocellulose”,
Chemcatchem.,
 2022, accepted,
 DOI:[10.1002/cctc.202101838](https://doi.org/10.1002/cctc.202101838)




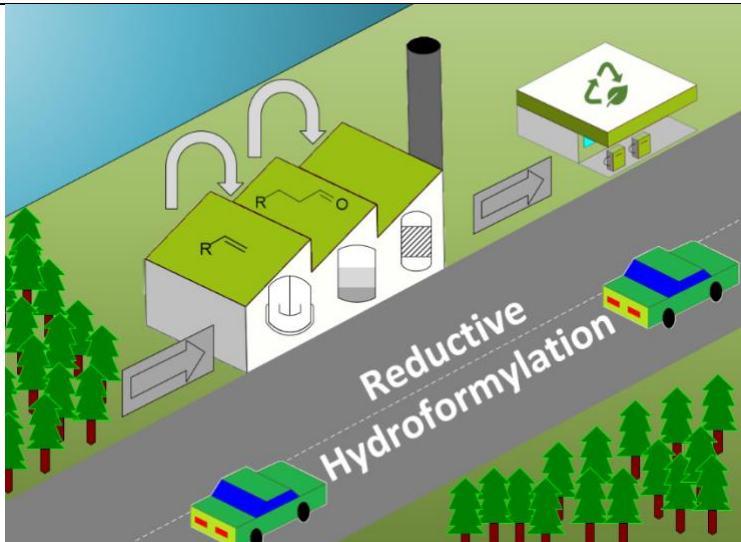
Heteropolyacids have been identified as promising for catalyzing the reaction types of hydration and dehydration, which play an important role in the valorization of lignocellulose. Not only do they possess adaptable Brønsted acidity, but they additionally show a redox multi functionality. To increase the industrial applicability of this promising class of catalysts and to enable recycling, many different approaches for immobilization (such as multiphasic catalysis or grafting) and solidification (such as salt formation) have been pursued in recent years. This review summarizes these efforts and highlights the studied acid-catalyzed lignocellulose conversions, trends and current challenges.


<p>91. M. Schrimpf, P. A. Graefe, A. E. Kaczyna, A. J. Vorholt*, W. Leitner “Measuring droplet sizes generated by 3D-printed stirrers in a lean gas-liquid-liquid system using borescopy”, <i>IC&E.</i>, 2022, 61, 7, 2701–2713, DOI: 10.1021/acs.iecr.1c03707 Highlighted as cover picture DOI: https://pubs.acs.org/toc/iecre/61/7.</p>	 <p>The figure shows 3D-printed stirrers (yellow) and a borescopy setup. A reflection module with a PC or FEP disc and a PTFE ring is used to observe droplets through a borescope. The borescopy images show droplets in a liquid system, with some highlighted in green.</p>
<p>Photo-optical probes with automated image analysis are among the most promising measurement techniques for gas-liquid-liquid systems, but literature on the application in lean water-in-oil dispersions is scarce. Taking water-in-1-octene as a model system, adhering droplets that severely cloud the images are successfully prevented using a polymeric disc made of polycarbonate or fluorinated ethylene propylene. Sharp bright-field imaging is enabled using a neither fully diffuse nor specular reflection pane. Various 3D-printed stirrers are characterized by their energy input, including gas-inducing modifications. Gas induction impairs the energy input of the stirrer and the imaging of droplets. Nevertheless, the measurement technique reliably provides droplet size distributions that exclude gas bubbles. Axial stirrers are preferable if one position at high stirring speeds is measured, as the homogeneity of droplet sizes along the reactor height is promoted. Radial stirrers are preferable if the stirring speed is varied, as the same trend of the droplets sizes is measurable along the reactor height. For radial stirring, the most beneficial position of the probe is close or slightly above the stirrer. The use of borescopy is thus found to be feasible if adhering droplets can be prevented and vision on droplets is not obstructed by too many bubbles.</p>	

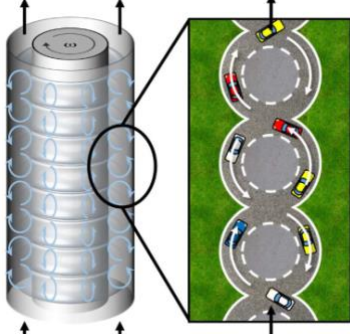
<p>90. S. Püschel, E. Hammami, K. R. Ehmann, T. Rösler, A. J. Vorholt*, W. Leitner “Auto-tandem catalytic reductive hydroformylation with continuous multiphase catalyst recycling”, <i>Catal. Sci. Tech.</i>, 2022, 12, 728 - 736, DOI: 10.1039/D1CY02000E Highlighted as cover picture DOI: 10.1039/D2CY90011D</p>	 <p>The diagram illustrates a two-reactor system. Reactor 1 (Cat. 1) converts an olefin (R-CH=CH2) into an aldehyde (R-CH2-CHO). Reactor 2 (Cat. 2) further reduces the aldehyde to an alcohol (R-CH2-CH2-OH). A Rh/amine catalyst is recycled between the reactors. The process is shown as a sustainable route from biomass to bio-fuels, with a bicycle and a car icon representing the final products.</p>
<p>The production of alcohols from olefin-enriched Fischer-Tropsch cuts represents a promising route to CO₂-neutral bio-synthetic fuels. Tandem-catalytic systems as alternative for the conventional two-step production of long-chain alcohols are attractive in terms of energy and resource efficiency. Herein, we present the first rhodium-based catalytic system capable of direct conversion of olefins to alcohols in a biphasic liquid/liquid system. After optimizing reaction conditions for the biphasic operation, an alcohol selectivity of up to 64% was achieved, while aldehydes and olefin isomers were observed as main byproducts. By the employment of water-soluble alkanolamines, the catalyst is immobilized in a water phase and can be easily separated from the product containing organic phase with rhodium loss as low as 0.1%. After investigation of various reaction parameters, a TON of 128 in batch operation was achieved. Furthermore, the developed catalyst recycling strategy was implemented in a continuously operated miniplant, reaching a TTON for alcohol production of 1236 after 50 hours.</p>	

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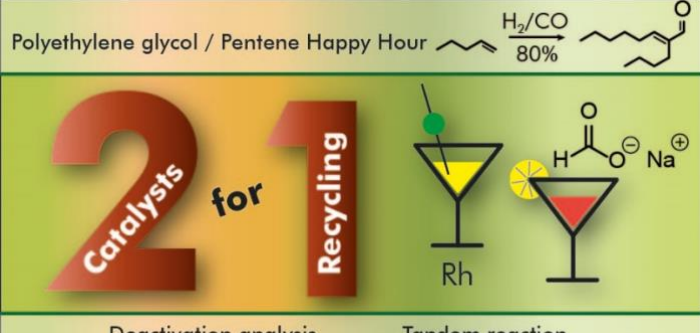
<p>89. H. Kreissl, J. Jin, S. Lin, D. Schütte, S. Störtte, N. Levin, B. Chaudret, A. J. Vorholt, A. Bordet and W. Leitner “Commercial Cu₂Cr₂O₅ Decorated with Iron Carbide Nanoparticles as Multifunctional Catalyst for Magnetically Induced Continuous Flow Hydrogenation of Aromatic Ketones”, <i>Angew. Chem.</i>, 2021, 60, 26639–26646, DOI: 10.1002/anie.20210791</p>	<p>Commercial copper chromite is decorated with iron carbide nanoparticles using a simple and versatile method, producing a magnetically activable multifunctional catalytic system. This system (ICNPs@Cu₂Cr₂O₅) is able to reduce aromatic ketones to aromatic alcohols when exposed to a high frequency alternating current magnetic field, i.e. magnetic induction. Under magnetic excitation, the ICNPs generate locally confined hot spots, activating selectively the Cu₂Cr₂O₅ surface while the global temperature of the reaction mixture remains low (~ 80°C). The ICNPs@Cu₂Cr₂O₅ catalyst selectively hydrogenates a scope of benzylic and non-benzylic ketones under these mild conditions (3 bar H₂, heptane), while ICNPs@Cu₂Cr₂O₅ or Cu₂Cr₂O₅ are inactive when the same global temperature is adjusted by conventional heating. A flow reactor is presented allowing the combined use of magnetic induction for continuous flow hydrogenation at elevated pressure. The excellent catalytic properties of ICNPs@Cu₂Cr₂O₅ for the hydrogenation of biomass-derived furfuralacetone are conserved for at least 17 hours on stream, demonstrating for the first time the application of a magnetically heated catalyst to a continuously operated hydrogenation reaction in the liquid phase. The reported approach for the decoration of solid materials with magnetically activated nanoparticles may be applied to a wide range of heterogeneous catalysts, generalizing the access to potential advantages associated with magnetic induction in catalysis.</p>
 <p>The figure shows a batch reactor and a continuous flow reactor. In the batch reactor, a catalyst (ICNPs@Cu₂Cr₂O₅) is used to hydrogenate an aromatic ketone (R-C(=O)-Ar) with H₂ (3 bar) under magnetic induction (μ₀H, f) to produce an aromatic alcohol (R-CH₂-OH-Ar). The continuous flow reactor setup is also shown, demonstrating the catalyst's performance over time.</p>	

<p>88. S. Püschel, S. Störtte, J. Topphoff, A. J. Vorholt*, W. Leitner “Green process design for reductive hydroformylation of renewable olefin cuts for drop-in diesel fuels”, <i>Chemsuschem</i>, 2021, 14,23, 5226-5234 DOI:10.1002/cssc.202100929.</p>	
<p>CO₂ neutral fuels are a way to cleaner and more sustainable mobility. Utilization of bio-syngas via Fischer-Tropsch (FT) synthesis represents an interesting route for the production of tailor-made biofuels. Recent developments in FT catalyst research led to olefin-enriched products, enabling the synthesis of alcohol-enriched fuels by reductive hydroformylation of the C=C double bond. Several alcohols have already proven to be suitable fuel additives with favorable combustion behavior. We investigated a hydroformylation-hydrogenation sequence of FT-olefin-paraffin mixtures as a potential route to alcohols. A liquid-liquid biphasic system with a rhodium/TPPTS catalyst system was chosen for effective catalyst recycling. After optimizing reaction conditions with a model substrate consisting of 1 octene and n heptane the conversion of an actual olefin-containing C5 C10 FT product fraction to alcohols in continuously operated processes for 37 hours has been achieved with total Turnover number of 23,679</p>	

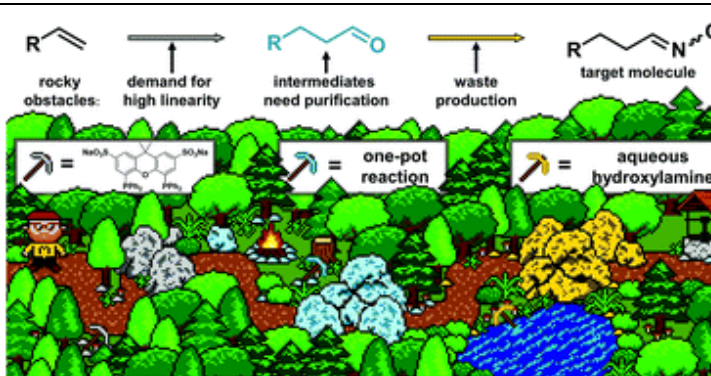
<p>87. T.Rösler, K.R.Ehmann, K.Köhnke, M.Leutzsch, N.Wessel, A.J.Vorholt*, W.Leitner “Reductive Hydroformylation With A Selective And Highly Active Rhodium Amine System”, <i>J. Catal.</i>, 2021, 400, 234-243 DOI: 10.1016/j.jcat.2021.06.001</p>	
<p>Direct synthesis of alcohols from olefins <i>via</i> reductive hydroformylation is important for various applications. Catalytic systems of rhodium in combination with tertiary amines are highly selective but have rarely been reported. Little is known about the role of tertiary amines or even if they act as ligands during the catalytic cycle. In this research, the role of the amine during those reactions was investigated in depth. As a model reaction, 1-octene was converted to 1-nonanol using a molecular rhodium catalyst in combination with various trialkylamines. Identification of important parameters such as the amine concentration and the carbon monoxide partial pressure hint that there is a susceptible equilibrium for the catalytically active species. A Tolman-like map was created in which the steric bulkiness and the basicity of employed amines was compared to the hydrogenation activity of the resulting reaction system. A clear dependency on steric and electronic constraints was found, which is typical for metal bound ligands. The nature of the catalyst was intensively studied via ¹³C- and ¹⁰³Rh-NMR during which the equilibrium of several anionic rhodium species was identified. <i>In situ</i> ¹H-NMR showed the presence of two major hydride species during the reaction. The equilibrium of those hydrides is heavily influenced by the nature of the applied amine indicating that it is essential for the hydride formation. Complementary <i>in situ</i> IR-experiments confirmed the formation of anionic rhodium species in presence of triethylamine with [Rh(CO)₄]⁻ being the major rhodium-carbonyl species.</p>	

<p>86. M. Schimpf, J. Esteban, H. Warmeling, T. Färber, A. Behr, A. J. Vorholt “Taylor-Couette reactor: Principles, design, and applications”, <i>AICHE</i> 2021, 67, e17228., DOI: 10.1002/aic.17228</p>	
<p>The Taylor-Couette reactor (TCR) is an apparatus that capitalizes on the Taylor-Couette flow, which allows many flow regimes and conditions to perform (bio-)chemical conversions with precise control of various reactor characteristics. With the possibility to continuously perfuse the reactor with a reaction medium, the TCR becomes interesting for chemical engineering applications. In this review, we introduce this reactor type and provide an overview of its history, principles of the flow regimes, and a description and design aspects of the reactors and their elements. Available information in the literature is summarized and harmonized to present available formulas and correlations in a consistent set of variables. Additionally, a wide number of applications in process technology are covered, including reactions in homogeneous, photo, and enzymatic catalysis, polymer synthesis, and crystallization and aggregation-flocculation processes. Focusing on this reactor configuration, this article intends to be used as a hub for scientific groups interested in TCRs.</p>	

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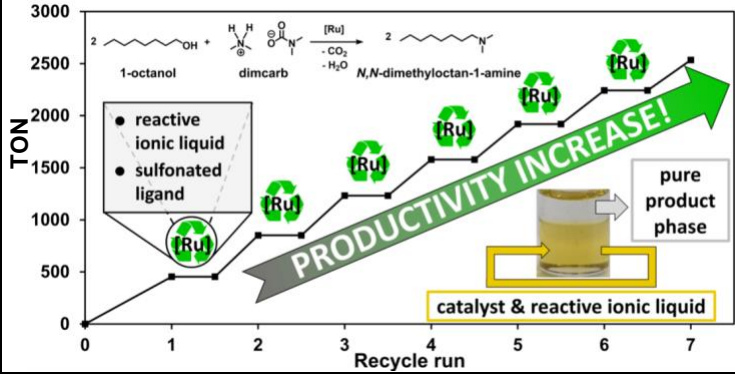
<p>85. M. Strohmam, J. T. Vossen, A. J. Vorholt*, W. Leitner “Recycling of Two Molecular Catalysts in the Hydroformylation/Aldol Condensation Tandem Reaction Using One Multiphase System”, <i>Green Chem.</i> 2020, 22, 8444-8451, DOI: 10.1039/D0GC03392H</p>	
<p>Tandem reactions are of great importance to efficiently execute multiple conversions in one synthesis step. Herein we present a multiphase system for the hydroformylation/aldol condensation, which is able to recycle both optimized catalysts multiple times. The system consists of an organometallic rhodium/sulfoxantphos hydroformylation catalyst and basic NaOH as aldol condensation initiator, which are both immobilized in a polyethylene glycol phase. Under reaction conditions, NaOH is converted to sodium formate, which is still able to catalyse the aldol condensation. The reaction and recycling are demonstrated by the conversion of 1 pentene to the corresponding aldol product in a recycling experiment. During nine consecutive runs, no significant loss of activity is found with an overall TON of 8700 in regard to the rhodium catalyst and an average rhodium leaching of only of 0.07% per run is observed.</p>	

84. M. Terhorst, C. Plass, A. Hinzmann, A. Guntermann, T. Jolmes, J. Rösler, D. Panke, H. Gröger, D. Vogt, A. J. Vorholt, T. Seidensticker
“One-pot synthesis of aldoximes from alkenes via Rh-catalysed hydroformylation in an aqueous solvent system”,
Green Chem.
 2020, **22**, 7974–7982, DOI: [10.1039/d0gc03141k](https://doi.org/10.1039/d0gc03141k)



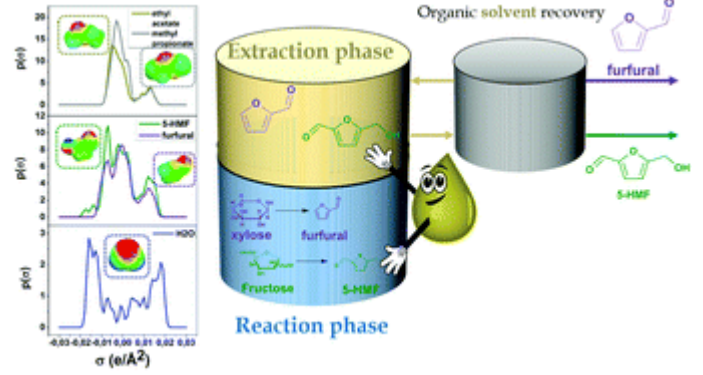
Aldoxime synthesis directly starting from alkenes was successfully achieved through the combination of hydroformylation and subsequent condensation of the aldehyde intermediate with aqueous hydroxylamine in a one-pot process. The metal complex Rh(acac)(CO)₂ and the water-soluble ligand sulfoxantphos were used as the catalyst system, providing high regioselectivities in the initial hydroformylation. A mixture of water and 1-butanol was used as an environmentally benign solvent system, ensuring sufficient contact of the aqueous catalyst phase and the organic substrate phase. The reaction conditions were systematically optimised by Design of Experiments (DoE) using 1-octene as a model substrate. A yield of 85% of the desired linear, terminal aldoxime ((E/Z)-nonanal oxime) at 95% regioselectivity was achieved. Other terminal alkenes were also converted successfully under the optimised conditions to the corresponding linear aldoximes, including renewable substrates. Differences of the reaction rate have been investigated by recording the gas consumption, whereby turnover frequencies (TOFs) >2000 h⁻¹ were observed for 4-vinylcyclohexene and styrene, respectively. The high potential of aldoximes as platform intermediates was shown by their subsequent transformation into the corresponding linear nitriles using aldoxime dehydratases as biocatalysts. The overall reaction sequence thus allows for a straightforward synthesis of linear nitriles from alkenes with water being the only by-product, which formally represents an anti-Markovnikov hydrocyanation of readily available 1-alkenes.

83. M. Terhorst, C. Heider, A. J. Vorholt, D. Vogt, T. Seidensticker
“Productivity leap in the homogeneous ruthenium-catalyzed alcohol amination through catalyst recycling avoiding volatile organic solvents”,
ACS Sustainable Chem. Eng.
 2020, **8**, 27, 9962–9967, DOI: [10.1021/acssuschemeng.0c03413](https://doi.org/10.1021/acssuschemeng.0c03413)



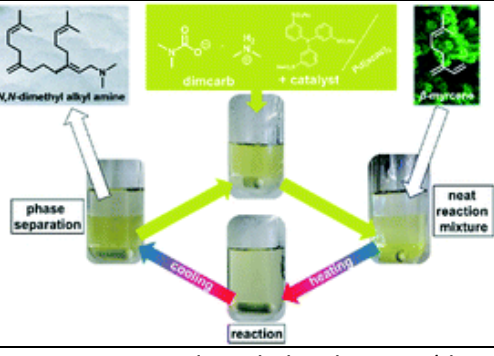
A reactive ionic liquid was successfully applied in the homogeneous ruthenium-catalyzed alcohol amination for the first time. Through detailed investigation of the phase behavior and the application of sulfonated ligands, a biphasic system was developed, which fulfils several key points of a sustainable process. This strategy allows, without use of additional volatile organic compounds, a pure product phase to be obtained, enabling the catalyst to be used in repetitive recycling runs. Hence, the productivity of the catalyst was increased fivefold to a cumulative TON of >2,500, which reflects a particularly high catalyst productivity for homogeneous ruthenium catalyzed alcohol amination.

82. J. Esteban, A.J. Vorholt*, W. Leitner
“An overview of the biphasic dehydration of sugars to 5-hydroxymethylfurfural and furfural: a rational selection of solvents using COSMO-RS and selection guides”,
Green Chem.
 2020, **22**, 2097–2128, DOI: [10.1039/C9GC04208C](https://doi.org/10.1039/C9GC04208C)

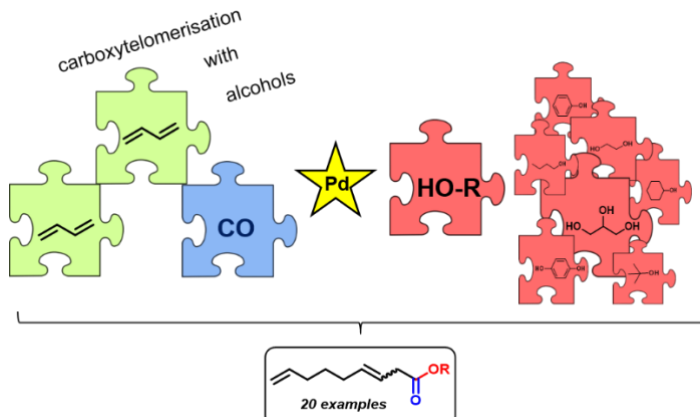


The valorization of sugars from lignocellulosic biomass has attracted much interest for the production of chemicals and fuels. From the dehydration of glucose or fructose and xylose, 5-hydroxymethylfurfural (5-HMF) and furfural can be obtained, respectively, which are highly praised chemicals used as building blocks. To increase the productivity of the process avoiding undesired side reactions that furans may undergo in the reaction phase, many authors follow a liquid–liquid approach. This way, an in situ extraction of the dehydration products occurs from the reaction phase (usually aqueous) to an organic solvent phase. Solvent selection is a matter of interest in Green Chemistry; therefore, careful consideration must be given to select the most appropriate alternatives in terms of performance, environmental, health and safety (EHS) impacts and subsequent downstream processing. For performance, the CONductor-like Screening MOdel for Real Solvents (COSMO-RS) has emerged as a tool to screen among different candidates based on structural information of the molecules. For EHS considerations, different solvent guides assist in the assessment of the most favourable alternatives. This review provides a comprehensive survey of the solvents and operational conditions employed in the biphasic dehydration of sugars to 5-HMF and furfural, followed by an account of the selection guides and methods for the evaluation of solvents, including COSMO-RS. Finally, to contrast with the most commonly selected solvents, such as methyl isobutyl ketone, a rational screening is presented here for the biphasic production of furans based on COSMO-RS predictions and the assessment of the selection guides.

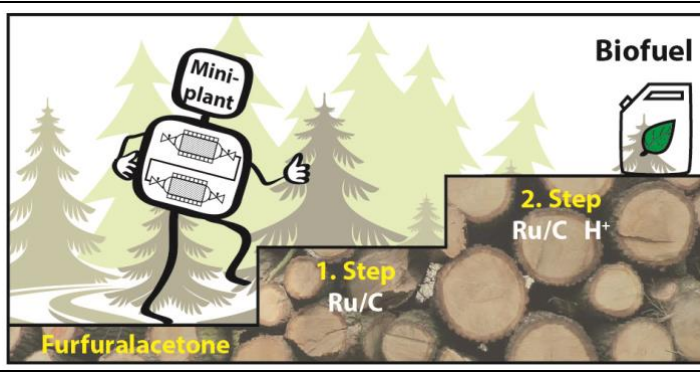
81. M. Terhorst, A. Kampwerth, A. Marschand, D., Vogt, A.J., Vorholt, T., Seidensticker,
“Facile catalyst recycling by thermomorphic behaviour avoiding organic solvents: a reactive ionic liquid in the homogeneous Pd-catalysed telomerisation of the renewable β-myrcene”,
Catal. Sci. & Tech.
 2020, **10**, 1827–1834, DOI: [10.1039/C9CY02569C](https://doi.org/10.1039/C9CY02569C)

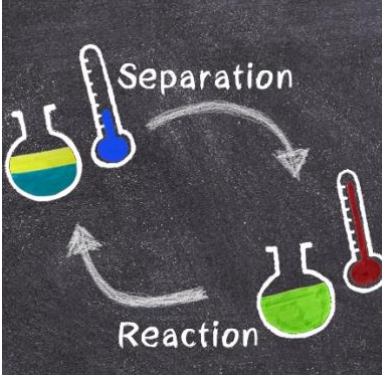



For the first time, the reactive ionic liquid *N,N*-dimethyl ammonium *N,N*-dimethyl carbamate (dimcarb) was used as a polar solvent in the palladium-catalyzed telomerisation of the renewable monoterpene β-myrcene. By doing so, it was possible to avoid any volatile organic solvents. Moreover, the special decomposition behaviour of the reactive ionic liquid dimcarb could be exploited to the extent that dimethyl amine was used as a reagent in the reaction. Accordingly, non-symmetrical C₂₀-chain dimethyl amines were produced from β-myrcene and dimethylamine liberated by dimcarb, achieving selectivities higher than 80%. Detailed investigations revealed the thermomorphic behaviour of the reaction mixture consisting only of dimcarb, β-myrcene and the catalytic system. The advantageous temperature-dependent phase behaviour resulted in one liquid phase occurring at the reaction temperature and two liquid phases upon cooling. Consequently, a virtually pure organic product phase could be separated from the polar catalyst-containing dimcarb phase. Immobilization of the catalyst in the polar reactive ionic liquid phase was ensured by the use of sulfonated triphenylphosphine derivatives. Subsequently, the separated catalyst-containing dimcarb phase was successfully reused in 14 consecutive recycling runs with only minimal leaching of both the catalyst and dimcarb, reaching a total turnover number of 12 000.

<p>80. D. Vogelsang, J. Vondran, K. Hares, K. Schäfer, T. Seidensticker, A. J. Vorholt* “Palladium catalysed acid-free Carboxytelomerisation of 1,3-Butadiene with Alcohols accessing Pelargonic Acid Derivatives including Triglycerides under selectivity control”, <i>Adv. Syn. & Catal.</i> 2020, 362, 3, 679-687 DOI: 10.1002/adsc.201901383</p>	
<p>Palladium catalysed carboxytelomerisation of 1,3-butadiene with alcohols yields unsaturated C₉-pelargonic esters in an atom-economic and straightforward way. Although carboxytelomerisation is of current interest, limitations of applicable alcohol substrates have not been fully investigated. In here, we present the transfer of the catalytic system comprising palladium acetate and tri-n-butyl phosphine in pyridine to a broad variety of 20 alcohols with vast difference in nucleophilicity and sterical demands yielding the corresponding esters in a 100 % atom economic manner. Effects of nucleophilicity and sterical demands were revealed for monoalcohols, di- and polyols. Whilst yields, chemoselectivity and E/Z-selectivity of the pelargonic acid derivatives were excellent with up to 99%, selectivity towards mono-, di- and triesters could be controlled successfully. Finally, the reaction profile of the carboxytelomerisation glycerol was uncovered, yielding up to 97% of industrially relevant unsaturated C₉-short chain fats</p>	

2019

<p>79. M. Strohmann, A. Bordet, A. J. Vorholt* and W. Leitner “Tailor-made biofuel 2-butyltetrahydrofuran from the continuous flow hydrogenation and deoxygenation of furfuralacetone”, <i>Green Chem,</i> 2019, , 21, 6299-6306, DOI: 10.1039/c9gc02555c</p>	
<p>In this work, we present the first continuous flow process to produce the tailored biofuel 2-butyltetrahydrofuran from renewable resources. In a two-step approach lignocellulose-derived furfuralacetone is first hydrogenated and then deoxygenated over commercial catalysts to form the desired product. Both reactions were studied independently in batch conditions. The transition to a continuous flow system was done and various parameters were tested in the miniplant. Both reactions were performed in a two-reactor-concept approach to yield the desired 2-butyltetrahydrofuran in a high yield directly from furfuralacetone.</p>	

<p>78. J. Bianga, K. U. Künnemann, T. Gaide, A. J. Vorholt, T. Seidensticker, J. M. Dreimann, D. Vogt “Thermomorphic Multiphase Systems - Switchable Solvent Mixtures for the Recovery of Homogeneous Catalysts in Batch and Flow Processes”, <i>Chemistry - A European Journal,</i> 2019, 25, 50, 11586-11608, DOI: 10.1002/chem.201902154</p>	
<p>Over the past 20 years, thermomorphic multiphase systems (TMS) have been used as a versatile and elegant strategy for the recovery and the recycling of homogeneous transition metal catalysts, in both batch scale experiments and continuous operated processes. TMS ensure homogeneous reaction in a monophasic reaction mixture at reaction temperature as well as the recovery of the homogeneous transition metal catalyst via liquid-liquid separation at lower separation temperature. This is achieved by using at least two solvents, which have a highly temperature sensitive miscibility gap. The suitability of commercially available solvents makes this approach highly interesting from an industrial point of view.</p> <p>For the first time the present article reviews all works in the area of TMS aiming at a concise and integral representation of this approach for homogeneous catalyst recovery. Besides the discussion of examples from literature, also the thermodynamic fundamentals of temperature dependent miscibility of solvents are presented. In addition, this review gives key indicators to compare different TMS approaches, for instance. In this way, new solvent combinations and in-depth research as well as improvements of existing approaches can be addressed and promoted.</p>	

<p>77. J. Esteban, H. Warmeling, A. J. Vorholt “Utilization of deep eutectic solvents based on choline chloride in the biphasic hydroformylation of 1-decene with rhodium complexes”, <i>Catalysis Communications,</i> 2019, 129, 105721, DOI: 10.1016/j.catcom.2019.105721</p>	
<p>The hydroformylation of 1-decene was conducted in a liquid-liquid system consisting of a deep eutectic solvent to enable recycling of the noble metal catalyst. Operation using different phosphine-based ligands was analyzed (Biphephos, Sulfoxantphos and TPPMS) testing five deep eutectic solvents (DES) as polar phases. These were based on choline chloride (ChCl) as hydrogen bond acceptor with glycerol (Gly), ethylene glycol, glycerol carbonate, 1,2-propanediol and urea (U) as hydrogen bond donors, all of renewable origin. Screening of DESs and ligands was made reutilizing the best, being ChCl:U, ChCl:Gly and again ChCl:U the best performing media using Biphephos, Sulfoxantphos and TPPMS, respectively.</p>	

<p>76. J. M. Dreimann, E. Kohls, H. F. W. Warmeling, M. Stein, L. F. Guo, M. Garland, T. N. Dinh, A. J. Vorholt “In-situ infrared spectroscopy as a tool for monitoring molecular catalyst for hydroformylation in continuous processes”, <i>ACS Catalysis</i>, 2019, 9, 5, 4308-4319, DOI: 10.1021/acscatal.8b05066</p>	
<p>Non-invasive in-situ monitoring of catalyzed chemical reactions can show and monitor the stability of the used catalyst and ensure a high yield of the desired chemical processes. This study showed that infrared measurements in transmission mode are able to detect active catalytic species and can show deactivation phenomena in batch reactions and continuously operated miniplants. Apart from the substrates and products, a number of catalytic intermediates appear to be in equilibrium exchange at reaction conditions and hence the deconvolution of multi-species spectra exhibits superimpositions of these species. Quantum chemical calculations support the structural identification of recorded vibrational spectra. This comparative study of ATR versus transmission and batch experiment versus continuously operated miniplant shows that transmission IR is capable of getting in-depth spectroscopic data which can be deconvoluted by BTEM. A distinct dosing strategy is important to get meaningful data on the molecular catalyst under process conditions. This study gives a unique perspective on in-situ spectroscopic infrared investigations in molecular catalysis and future process control.</p>	


<p>75. C. Plass, A. Hinzmann, M. Terhorst, W. Brauer, K. Oike, H. Yavuzer, Y. Asano, A. J. Vorholt, T. Betke, H. Gröger “Approaching Bulk Chemical Nitriles from Alkenes: A Hydrogen Cyanide-Free Approach through Combination of Hydroformylation and Biocatalysis”, <i>ACS Catalysis</i>, 2019, 9, 6, 5198-5203, DOI: 10.1021/acscatal.8b05062</p>	
<p>A current challenge in catalysis is the development of novel catalytic methodologies for the production of bulk chemicals needed on multi-ten/hundred-thousands of tons per year with the requirement to be produced at very low costs often being in the single-digit US-\$ range. At the same time such novel methodologies should avoid drawbacks of current manufacturing processes. Addressing this research issue, a cyanide-free approach towards aliphatic nitriles used as industrial bulk chemicals was developed starting from readily accessible n-alkenes as starting materials available in bulk quantities. This chemoenzymatic process concept is exemplified for the synthesis of n-nonanenitrile and runs in water at low to moderate temperatures without the need for any types of cyanide sources. The process is based on a combination of a metal-catalyzed hydroformylation as the world-leading production technology for aldehydes with an emerging enzyme technology, namely the recently developed transformation of aldoximes into nitriles through dehydration by means of aldoxime dehydratases. As a missing link an efficient aldoxime formation with subsequent removal of excess of hydroxylamine as enzyme-deactivating component was found which enabled to merge these three steps hydroformylation, aldoxime formation and enzymatic dehydration towards a nitrile synthesis without the need for purification of intermediates.</p>	

<p>74. M. Schrimpf, J. Esteban, T. Rösler, A. J. Vorholt*, W. Leitner “Intensified Reactors for Gas-Liquid-Liquid Multiphase Catalysis: from Chemistry to Engineering”, <i>Chemical Engineering Journal</i>, 2019, 372, 917-939, DOI: 10.1016/j.cej.2019.03.133</p>	
<p>Biphasic liquid-liquid and particularly gas-liquid-liquid (GLL) environments are used in many chemical transformations performed by homogeneous catalysts where they have proven very effective for catalyst recycling, greatly improving the economy of using costly organometallic catalyst complexes such as for hydroformylation. Reacting GLL systems suffer from mass transfer limitations, for which intensified contacting is necessary to enhance the reaction rate. To tackle this issue, process intensified reactors have been designed and developed throughout the years to create large interfacial areas and high mass transfer coefficients. Apart from the classic continuously stirred tank reactor, setups like static mixer reactors, ejector loop reactors, and microreactors are promising alternatives that have gained momentum throughout the last years. This critical review covers the basic aspects of GLL mass transfer and a discussion on a number of reactions in this type of environment. More extensively, the current state of the art of contacting equipment for intensified GLL operation is described, including aspects of reactor design and correlations for different operating conditions.</p>	

<p>73. R. Kuhlmann, K. U. Künnemann, L. Hinderink, A. Behr, and A. J. Vorholt, “CO₂ based synthesis of various formamides in miniplant scale: a two-step process design”, <i>ACS Sustainable Chem. Eng.</i>, 2019, 7, 5, 4924-4931, DOI: 10.1021/acssuschemeng.8b05477</p>	
<p>The utilization of carbon dioxide in the synthesis of valuable chemicals has attained high attention in the last decades. Numerous new syntheses were developed by applying innovative catalysts and demonstrated the versatile application possibilities of the thermodynamic stable molecule. However, only few reaction systems were developed into a technical application. In this work, we present investigations of a homogeneous catalyzed reaction system for the synthesis of formamides in a miniplant scale. The applied catalyst complex Ru-Macho was recycled via immobilization in a nonpolar alcohol phase and showed a high stability within the observed period of 234 hours. The formed products were extracted in-situ into an aqueous phase. An average yield of 48% N,N-dimethylformamide (DMF) proved a good activity of the reaction system. An alteration of the reaction designed into a two-step process allowed an extension of the product range to yield a broad variation of formamides with high yields up to 89%.</p>	

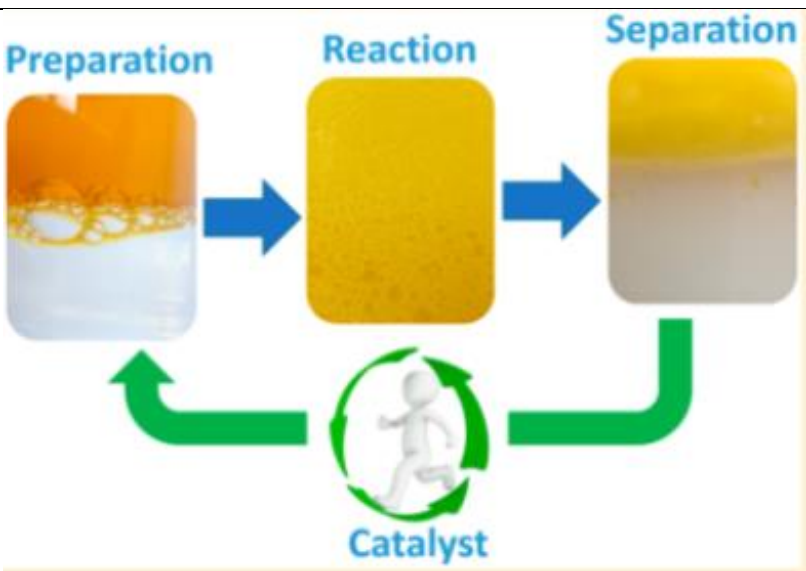
72. T. A. Faßbach, A. J. Vorholt* and W. Leitner, **“The Telomerization of 1,3 Dienes – A Reaction Grows Up”**, *ChemCatChem*, 2019, 11, 4, 1153-1166, DOI: [10.1002/cctc.201801821](https://doi.org/10.1002/cctc.201801821)

Highlighted as cover picture DOI: [10.1002/cctc.201900192](https://doi.org/10.1002/cctc.201900192)



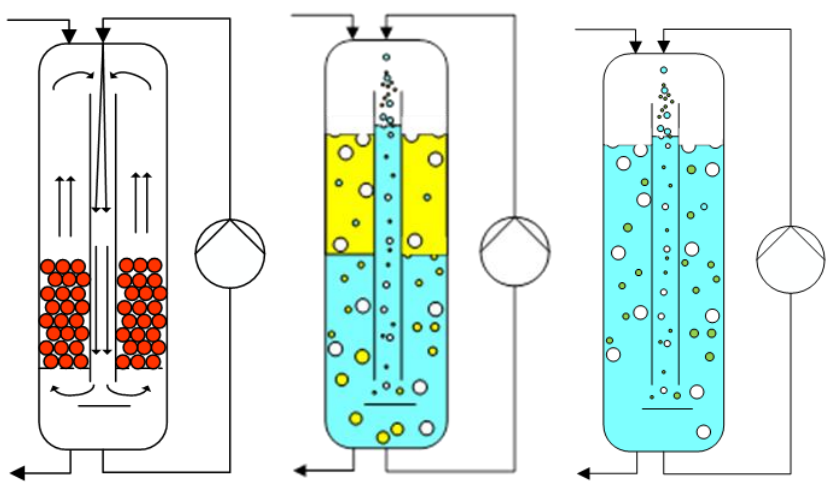
Telomerization is a versatile tool for synthesizing unsaturated ethers, amines and other molecules starting from 1,3 dienes and respective nucleophiles. The homogeneously catalyzed reaction has been the subject of academic and industrial research for over 50 years, offering a broad variety of substrates, catalysts and process concepts. This review presents the advances and developments in this field over the last decade. The focus was on the conversion of renewable resources, the synthesis of promising new products and the development of efficient process concepts to combine these.

71. T. Rösler, T. A. Faßbach, M. Schimpf, A. J. Vorholt,* and W. Leitner, **“Toward Water-Based Recycling Techniques: Methodologies for Homogeneous Catalyst Recycling in Liquid/Liquid Multiphase Media and Their Implementation in Continuous Processes”**, *Ind. Eng. Chem. Res.*, 2019, 58 (7), 2421–2436, DOI: [10.1021/acs.iecr.8b04295](https://doi.org/10.1021/acs.iecr.8b04295)



Biphasic water-based solvent systems offer the opportunity of efficient recycling of homogeneous catalysts. Water separates well from most organic solvents; therefore, water-soluble catalysts can be immobilized in this phase. Furthermore, water can substitute hazardous and environmentally unfriendly organic solvents in these systems. Within industry only the Ruhrchemie/Rhône-Poulenc process uses plain water to immobilize the homogeneous catalyst for the hydroformylation of propene. Yet for more hydrophobic substrates, no water-based system has been commercialized. This review will summarize recent developments in the field of water-based recycling systems. Topics in this field are intensification of the mixing process, the use of thermomorphic solvent systems, and the employment of several additives, like alcohols and surfactants. Continuous operated processes for these recycling strategies will be presented and discussed.

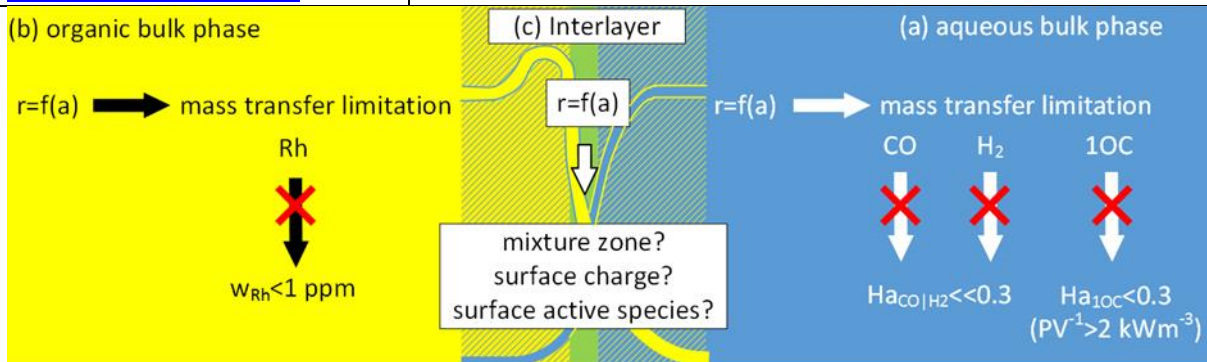
70. J. Dreimann, A. Behr and A. J. Vorholt, **“Strahldüsenreaktoren”**, *Handbuch Chemische Reaktoren*, Ed. W. Reschetilowski., Springer, 2019, DOI: [10.1007/978-3-662-56444-8](https://doi.org/10.1007/978-3-662-56444-8)



Dieses Kapitel informiert kurz über die theoretischen Grundlagen des Freistrahlsreaktors und des Strahldüsenumlaufreaktors (Jet-Loop-Reaktor). Die Vor-teile dieser Reaktoren werden an Bei-spielen aus der heterogenen und homogenen Katalyse sowie aus der Biokatalyse erläutert.

69. J. Esteban, H. Warmeling, A. J. Vorholt, **“An approach to chemical reaction engineering and process intensification for the lean aqueous hydroformylation using a jet loop reactor”**, *CIT*, 2019, 91, 5, 1–8, DOI: [10.1002/cite.201800137](https://doi.org/10.1002/cite.201800137)


The biphasic hydroformylation of 1-octene using a lean aqueous phase as solvent phase for catalyst recycling is discussed here. The gas-liquid-liquid reaction was homogeneously catalyzed by industrial standard catalytic system with $[\text{Rh}(\text{cod})\text{Cl}]_2$ as precursor and TPPTS as ligand. This work summarizes investigations addressing different aspects of the reaction, where a procedural approach was followed to gain understanding of its nature, kinetics and interphase reactivity. Finally, the application of the jet loop reactor as means to intensify the reaction is analyzed.



2018

68. D. Vogelsang, M. Dittmar, T. Seidensticker, A. J. Vorholt, "Palladium-catalysed carboxytelomerisation of β -myrcene to highly branched C₂₁-esters", *Catal. Sci. & Tech.*, 2018, 8, 4332-4337, DOI: [10.1039/C8CY00769A](https://doi.org/10.1039/C8CY00769A)

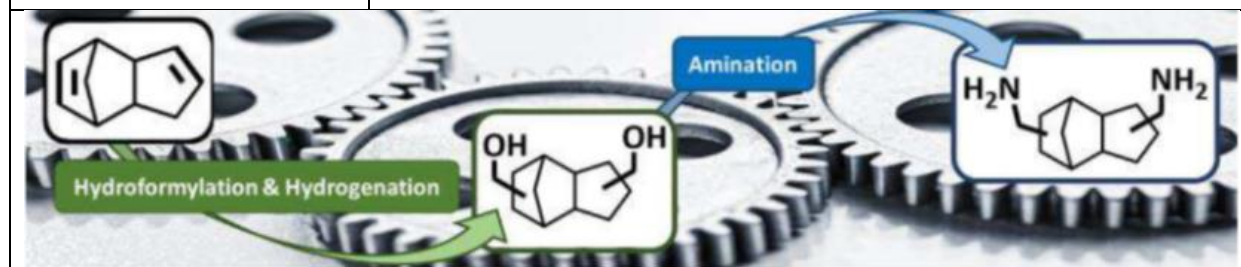
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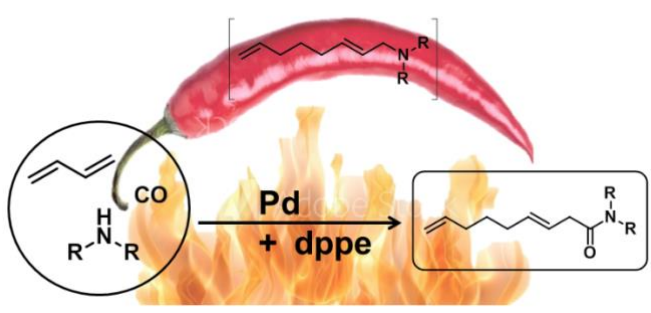
The palladium-catalysed carboxytelomerisation of a branched 1,3-diene with alcohols is herein presented. By applying the renewable β -myrcene as a model substrate, an access to highly branched industrially relevant C₂₁-esters in a 100% atom economic way is thereby established. Based on a detailed investigation on the influence of different monophosphine ligands, the Tolman angle was determined as a crucial factor for high chemoselectivity towards the desired ester products. Additionally, through the comprehensive design of experiments (DoE), significant reaction parameters were identified leading to optimised reaction conditions for methanol as nucleophile. Finally, the generality of these optimised reaction conditions was proven by applying eight different alcohols yielding in highly branched esters with yields up to 99% and excellent chemoselectivities.

67. S. Fuchs, D. Lichte, T. Jolmes, T. Rösler, G. Meier, H. Strutz, A. Behr, A. J. Vorholt, "Synthesis of industrial primary diamines via intermediate diols - combining hydroformylation, hydrogenation and amination", *ChemCatChem*, 2018, 10, 18, 4126-4133 DOI: [10.1002/cctc.201800950](https://doi.org/10.1002/cctc.201800950)

A homogenous transition metal catalysis that combines hydroformylation, hydrogenation and direct amination presents an elegant multi-step pathway for synthesising primary diamines from olefins and ammonia. The valuable intermediate TCD-diamine is obtained, which has a wide range of industrial applications as a monomer building block. The rhodium-catalysed hydrohydroxymethylation step converts non-conjugated dienes to the intermediate diols. Ammonia is added in a second ruthenium-catalysed amination step to obtain primary diamines. The conditions for both reactions were first optimised independently and combined to design a tandem reaction. For the amination reaction of the diol, excellent diamine yields of up to 88% in toluene were achieved. An analysis of the interactions between the two catalytic systems demonstrated that the conditions of both single reaction steps counteract each other, meaning the presence of either rhodium or ruthenium blocks the other respective reaction. Using a two-step approach, optimised reaction conditions were applied to achieve equally high diamine yields of 88%.

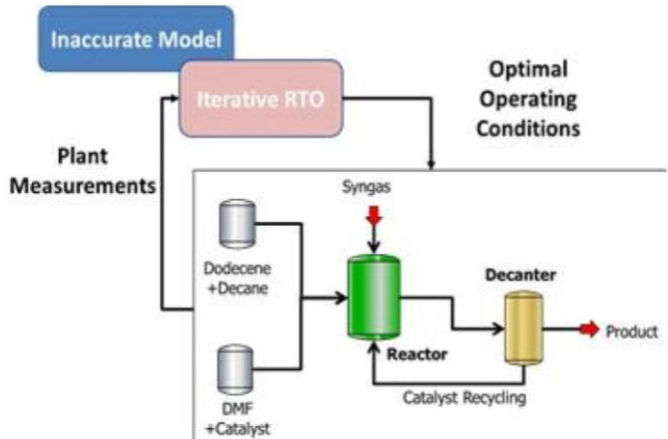


66. D. Vogelsang, J. Vondran, A. J. Vorholt, "One-Step Palladium Catalysed Synthetic Route to unsaturated Pelargonic C₉-Amides directly from 1,3 Butadiene", *J. Catal.*, 2018, 365, 24-28, DOI: [10.1016/j.jcat.2018.06.004](https://doi.org/10.1016/j.jcat.2018.06.004)



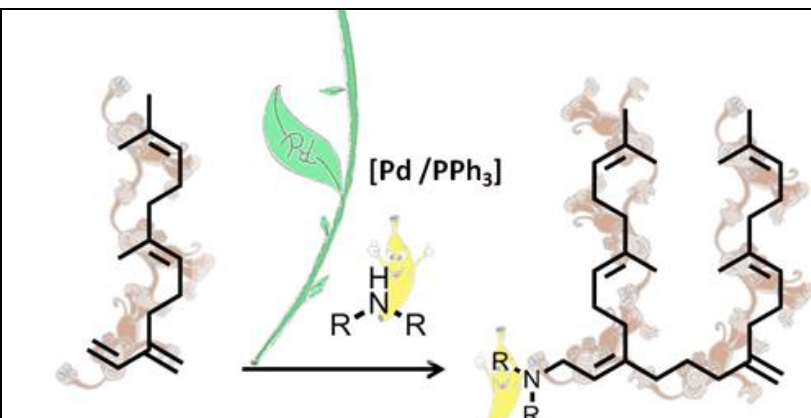
The first example of the palladium catalysed amidotelomerisation is presented, in style of the ambitious carboxytelomerisation. A straightforward synthetic tool was generated to produce several industrial relevant pelargonic C₉-amides based on the fundamental chemical feedstocks: 1,3-butadiene, carbon monoxide and secondary amines. The reaction network was uncovered and crucial influences were determined by design of experiments (DoE). Through the incorporation of an auto-tandem palladium acetate / diphenylphosphino ethane catalytic system, very good yields up to 77% of the desired amides and excellent selectivities of carbonylation products of 94% were achieved. The application of the amidotelomerisation conditions to different classes of amines offered a broad range of the corresponding pelargonic C₉-amides. Understanding the tandem catalysis, significant inhibition factors were uncovered and through a stepwise optimisation, for the first time a carbonylation reaction of octadienyle amines (telomer products) was shown, yielding in 99% of the desired linear pelargonic C₉-amide.

65. R. Hernandez, J. M. Dreimann, A. J. Vorholt, A. Behr, S. Engell, "An Iterative Real-time Optimization Scheme for the Optimal Operation of Chemical Processes under Uncertainty. Proof of Concept in a Miniplant", *Ind. Eng. Chem. Res.*, 2018, 57 (26), 8750-8770 DOI: [10.1021/acs.iecr.8b00615](https://doi.org/10.1021/acs.iecr.8b00615)



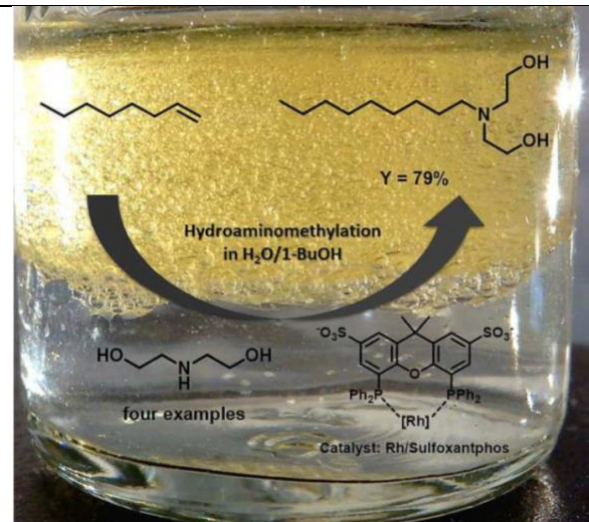
Real-time Optimization (RTO) has gained growing attention during the last few years as a useful approach to boost process performance while safety and environmental constraints are satisfied. Despite the increasing acceptance of RTO in traditional industries such as petrochemical and refineries, its application to novel chemical processes remains limited. This can be partially explained by the fact that only inaccurate models are available and the performance of the traditional RTO scheme suffers in the presence of plant-model mismatch. During the last few years, the so-called modifier-adaptation schemes for real-time optimization have been gaining popularity as an efficient tool to handle plant-model mismatch. So far, there are only few published works regarding experimental implementations. In this contribution, a reliable RTO scheme which is able to deal with model uncertainty and measurement noise is applied to a novel transition metal complex catalyzed process that is performed in a continuously operated miniplant. The experimental results show that the proposed scheme is able to drive the process to an improved operation despite significant plant-model mismatch demonstrating the applicability of the method to real processes.

64. D. Vogelsang, T. A. Faßbach, P. P. Kossmann, A. J. Vorholt, **“Terpene-Derived Highly Branched C₃₀-Amines via Palladium-Catalysed Telomerisation of β-Farnesene”,** *Adv. Syn Catal.*, 2018, 360, 10, 1984-1991 DOI: [10.1002/adsc.201800089](https://doi.org/10.1002/adsc.201800089)



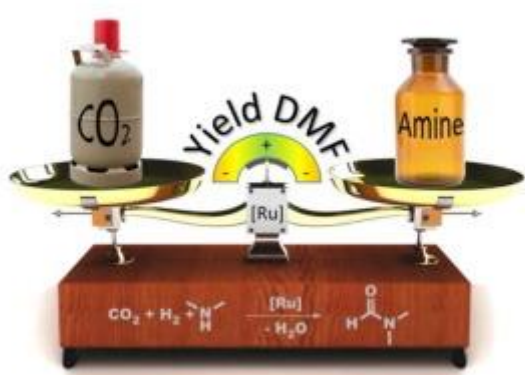
The synthesis of highly branched long chain amines in one step is still a challenge. The palladium catalysed telomerisation of the renewable sesquiterpene b-farnesene with secondary amines gives a new reaction pathway, which was investigated. Preliminary, a suitable palladium catalyst system was developed by a high-throughput screening. It efficiently allows for the synthesis of tertiary amines with a highly branched C₃₀-carbon chain. A yield of 94% for the desired allylic C₃₀-amines was achieved. The scope of feasible amines was expanded to thirteen amines with linear and branched alkyl and aryl groups. A correlation between the scaffold of the amine, basicity and the activity as nucleophile in the telomerisation reaction was uncovered. Based on the different polarities of the nonpolar in-situ formed C₃₀-substituted amines and the polar solvent, a proof of concept for catalyst recovery by simple decantation was shown.

63. T. A. Faßbach, F. O. Sommer, A. J. Vorholt **„Hydroaminomethylation in Aqueous Solvent Systems – An Efficient Pathway to Highly Functionalized Amines”,** *Adv. Syn Catal.*, 2018, 360, 7, 1473-1482, DOI: [10.1002/adsc.201701463](https://doi.org/10.1002/adsc.201701463)



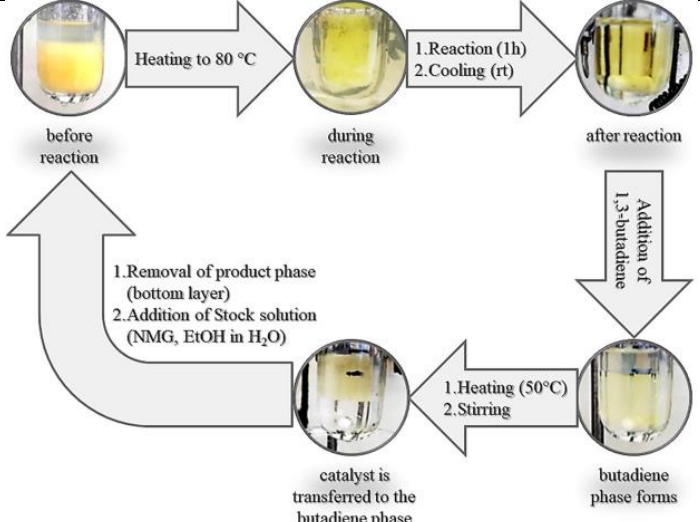
The tandem-catalyzed hydroaminomethylation is a useful tool to synthesize linear amines from olefins and amines in an atom efficient manner. To enable the coupling of highly functionalized, hydrosoluble amines with non-water-soluble olefins, this reaction must be transferred to aqueous biphasic solvent systems. In this work, we systematically evaluate reaction conditions to provide a selective hydroaminomethylation of 1-octene with diethanolamine as model substrates. Although water is both the condensation side product and the solvent, yields of 79% were achieved using a catalytic system consisting of [Rh(cod)Cl]₂ and sulfo-XantPhos. This approach was applied to other functionalized amines, proving this concept a suitable tool for the catalytic alkylation of highly functionalized amines.

62. R. Kuhlmann, M. Nowotny, K. U. Künnemann, A. Behr, A. J. Vorholt, **„Identification of key mechanics in the ruthenium catalyzed synthesis of N,N-dimethylformamide from carbon dioxide in biphasic solvent systems”,** *J. Catal.*, 2018, 361, 45-50, DOI: [10.1016/j.jcat.2018.02.006](https://doi.org/10.1016/j.jcat.2018.02.006)



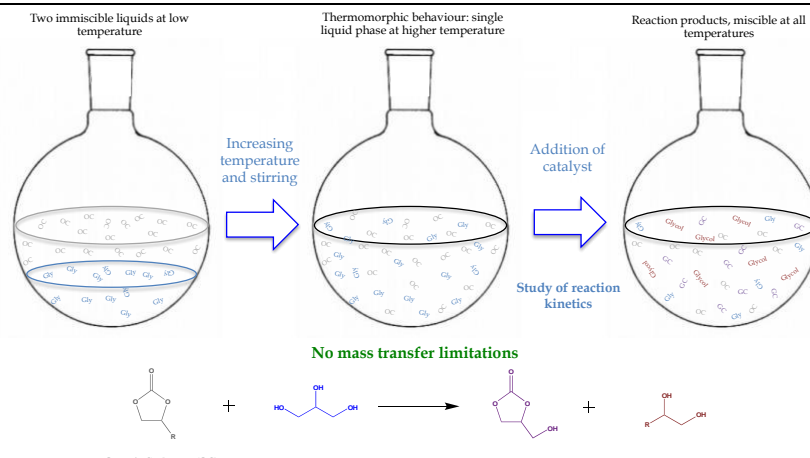
The identification of crucial key factors in the homogeneously catalyzed synthesis of *N,N*-dimethylformamide (DMF) from carbon dioxide with an integrated catalyst recycling is demonstrated in this work. All investigations were performed in a biphasic solvent system consisting of an aqueous phase and an aliphatic alcohol in order to evaluate the reaction performance with an integrated catalyst recycling. While no mass transfer limitations between both liquid phases could be identified, the main rate limiting factor for the carbon dioxide conversion could be located in the amine to carbon dioxide ratio. A conventional dosage of CO₂ via pressurization led to high CO₂ loadings that resulted in a low basicity and thus in poor yields up to 34% after 5 h. By adding carbon dioxide via reactive absorption into an aqueous amine phase a defined amount could be applied and the yield for the formamide increased up to 81%.

61. T. A. Faßbach, S. Püschel, A. Behr, S. Romanski, D. Leinweber, A. J. Vorholt **„Towards a Process for the Telomerization of Butadiene with N-Methylglucamine”,** *CES*, 2018, 181, 18, 122-131, DOI: [10.1016/j.ces.2018.02.012](https://doi.org/10.1016/j.ces.2018.02.012)




The telomerisation of 1,3-dienes with functionalized nucleophiles presents an atom efficient and selective synthesis of potential non-ionic surfactants. Crucial for application of these synthetic pathways is the effective recycling of the homogeneous palladium catalyst. In this work, we present the telomerisation of 1,3-butadiene with the renewable aminopolyol *N*-methylglucamine to a non-ionic surfactant in an aqueous solvent system. In order to achieve phase separation, the addition of freshly added 1,3-butadiene instead of an additional solvent offers an elegant way of catalyst recycling. With this method, recycling of the catalyst is feasible; a total turnover number of 1456 was reached.

60. J. Esteban, A. J. Vorholt
„Obtaining glycerol carbonate and glycols using thermomorphic systems based on glycerol and cyclic organic carbonates: kinetic studies“,
J. Ind. & Eng. Chem.,
 2018, 63, 124-132 DOI:
[10.1016/j.jiec.2018.02.008](https://doi.org/10.1016/j.jiec.2018.02.008)



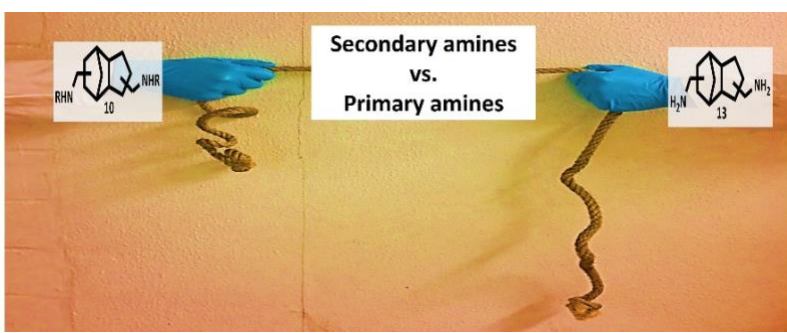
As a means to exploit the wide availability of glycerol (by-product of biodiesel), the production of valuable chemicals has emerged as an opportunity. Glycerol carbonate is one of such value-added products, whose synthesis has mostly been performed by transesterification of glycerol with dimethyl carbonate and, to a lesser extent, ethylene carbonate. Here we propose yielding glycerol carbonate by the same type of reaction, although using propylene and butylene carbonate as cosubstrates with glycerol making use of inexpensive Na_2CO_3 as catalyst. The systems glycerol and propylene carbonate as well as glycerol and butylene carbonate show limited miscibility at room temperature, constituting dispersion upon stirring. However, these two systems exhibit thermomorphic behaviour, i.e., they become fully miscible exceeding a certain temperature. In this work, we first evaluated this behavior on batches of both systems with different proportions of the glycerol and the corresponding organic carbonate. Then, we capitalized on this feature operating above the critical solution temperature to avoid possible mass transfer limitations instead of using solvents, as is common practice. Then, a study of the kinetics of both reactions was conducted, reaching the conclusion that potential models of overall second order with the catalyst showing some deactivation represented well the observed data.

59. D. Vogelsang, B. A. Raumann, K. Hares, A. J. Vorholt
„From Carboxytelomerization of 1,3-Butadiene to linear C10-Diester - Combinatoric Approaches for an efficient synthetic Route“,
Chem. Eur. J.,
 2018, 24, 9, 2264–2269, DOI:
[10.1002/chem.201705381](https://doi.org/10.1002/chem.201705381)



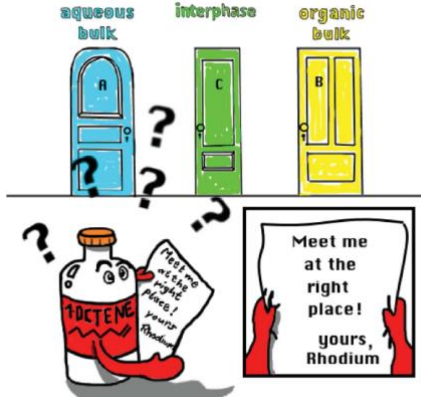
Two novel reaction pathways were tested to synthesize the linear α,ω -C10-diester exclusively from three basic chemical: 1,3-butadiene, carbon monoxide and methanol. Therefore, carboxytelomerization of 1,3-butadiene and methanol was merged with methoxycarbonylation in two different ways to obtain highly linear C10-diester. Through a palladium based assisted tandem catalytic system, 22% yield of the desired C10-diester was obtained without isolating the intermediates. Subsequently, the limitations of the novel assisted tandem catalytic concept were uncovered and based on that a two-step reaction regime was established. By optimization of the carboxytelomerization, the C9-monoester as intermediate could be formed in nearly quantitative yields and excellent linearity. In a second reaction step, the isolated monoester was successfully converted by methoxycarbonylation into the desired linear C10-diester in overall yields up to 84%

58. S. Fuchs, T. Rösler, B. Grabe, A. Kampwerth, G. Meier, H. Strutz, A. Behr, A. J. Vorholt,
“Synthesis of primary amines via linkage of hydroaminomethylation of olefins and splitting of secondary amines”,
Appl. Catal.,
 2018, 550, 198-205, DOI:
[10.1016/j.apcata.2017.11.010](https://doi.org/10.1016/j.apcata.2017.11.010)



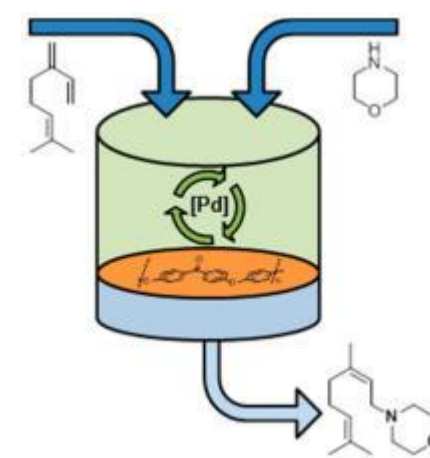



An elegant method capable of synthesising primary amines from olefins is presented by new orthogonal tandem amination reaction. Rh/Ru-catalysed bis-hydroaminomethylation of dienes towards secondary amines and primary amines is implemented. With the bis-splitting method intermediate secondary amines are converted to primary amines through subsequent addition of ammonia. Influences on the orthogonal catalytic system towards the formation of primary amines are discussed and point towards a novel N-dealkylation and alkylation mechanism. For the model substrate dicyclopentadiene (dcpd) yields of up to 29% of the primary TCD-diamine (3(4),8(9)-bis(aminomethyl)-tricyclodecane) were achieved under optimized conditions, with primary amine to secondary amine ratio of 5.8. The reverse reaction towards secondary amines was revealed as the limiting factor in the selective reaction towards primary amines caused by the equilibrium of the reaction. In this equilibrium, however, a slight tendency towards the primary amine was identified.

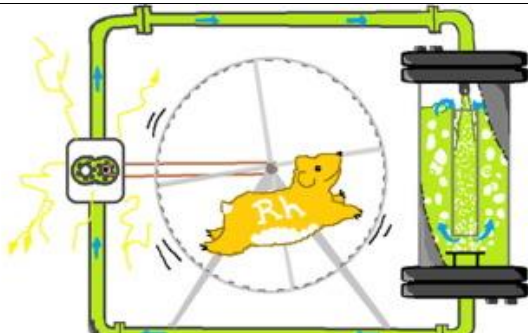
57. H. Warmeling, A.-C. Schneider and A. J. Vorholt,
“Considerations on film reactivity in the aqueous biphasic hydroformylation”,
AIChE J.,
 2018, 64, 1, 161–171, DOI:
[10.1002/aic.15884](https://doi.org/10.1002/aic.15884)

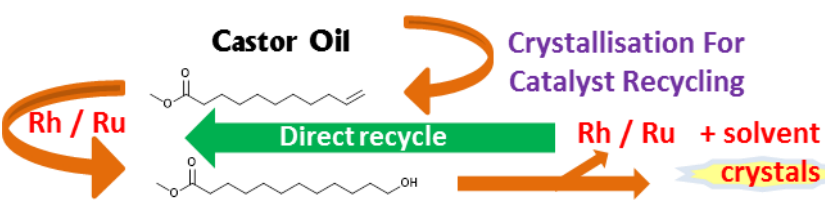


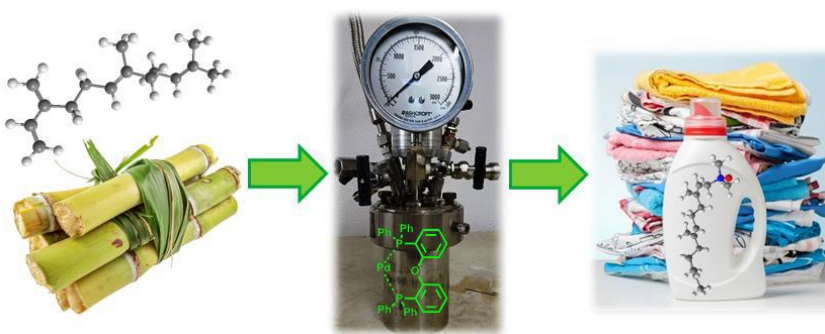
In experiments and kinetic models it was shown that the reaction rate of the biphasic aqueous hydroformylation of 1-octene is linear dependent on the created interfacial area. This phenomenon is directly linked to the question whether the reaction takes place in the bulk phase and is mass transfer limitation or at the surface which would mean an increase of reaction space. To evaluate the place of reaction a mass transfer analysis has been carried out. No mass transfer limitation for the gaseous components carbon monoxide and hydrogen as well as the olefin 1-octene was determined for the aqueous catalyst phase by calculating the Hatta numbers. With this observation it is possible to exclude the mass transfer as a potential influence and hence the aqueous bulk as the place of reaction. Thus the reaction is most probably surface active. This can be either explained the increase in film volume fraction where non-polar substrate as well as polar catalyst complex is present or through an increased catalyst concentration at the surface through dipole moment fluctuations.


2017


<p>56. D. Vogelsang, J. M. Dreimann, D. Wenzel, L. Peeva, J. da Silva Bungal, A. G. Livingston, A. Behr, and A. J. Vorholt "Continuously Operated Hydroamination – Toward High Catalytic Performance via Organic Solvent Nanofiltration in a Membrane Reactor", <i>Ind Eng Chem Res.</i> 2017, 56 (46), 13634–13641 DOI: 10.1021/acs.iecr.7b03770</p>	
<p>Still, the hydroamination of dienes to form allylic amines is a challenging task in a continuous operation. Herein, we present the performance of a membrane reactor by the implementation of a continuously operated hydroamination reaction of β-myrcene with morpholine. Via application of a poly ether-ether-ketone (PEEK) membrane, operation at elevated temperatures was possible in an integrated reaction/separation unit. First, the kinetics of the hydroamination reaction and relevant membrane characteristics were determined under optimized reaction conditions. Afterward, these results were incorporated in a reactor/separator model to predict the process behavior. With this, catalyst replenishment was adjusted resulting in stable continuous operation. In the end an increase of the turnover number from 460 to 5135 compared to a batch process was achieved. The desired geranyl amines were obtained in very good yields higher than 80%, while an excellent conversion of β-myrcene above 93% was reached in a long-time stable process.</p>	
<p>55. T. A. Faßbach, R. Kirchmann, A. Behr, A. J. Vorholt, "Recycling of homogeneous catalysts in reactive ionic liquid – solvent-free aminofunctionalizations of alkenes", <i>Green Chem.</i>, 2017, 19, 5243-5249 DOI: 10.1039/C7GC02272G</p>	
<p>The catalyst in homogeneously catalyzed aminofunctionalizations is often difficult to recycle, making these reactions expensive on an industrial scale. The use of dimethylammonium dimethylcarbamate (dimcarb) as a reactive ionic liquid provides an elegant solution to this challenge, as it is a substrate and polar phase at the same time. In this work, homogeneously transition-metal catalyzed reactions – specifically hydroamination, telomerization and hydroaminomethylation – are carried out in neat substrates without additional solvents. The ionic character of dimcarb enables the immobilization of the active catalysts in the reactive ionic liquid, using sulfonated ligands. Investigations regarding the hydroamination of 1,3-dienes led to a total turnover number (TON) of more than 8700 with β-farnesene in 12 repetitive recycling experiments. The telomerization of 1,3-butadiene was carried out over 30 consecutive runs without any loss of activity, resulting in a TTON of more than 90 000.</p>	
<p>54. R. Kuhlmann, A. Prüllage, K. Künnemann, A. Behr, A.J. Vorholt, "Process development of the continuously operated synthesis of N,N-dimethylformamide based on carbon dioxide", <i>J. CO2 Utilization</i>, 2017, 22, 184-190 DOI: 10.1016/j.jcou.2017.10.002</p>	
<p>The development of a process concept for the carbon dioxide based synthesis of N,N-dimethylformamide (DMF) is presented in this paper. Investigations were performed with a ruthenium catalyst comprising RuCl_3 hydrate as precursor and BISBI (2,2'-bis(diphenylphosphinomethyl)-1,1'-biphenyl) as ligand. A previously developed recycling concept where the catalyst complex was immobilized in 2-ethylhexan-1-ol was transferred from lab-scale into a continuously operated miniplant in order to evaluate stability, selectivity and recyclability of the catalyst. The results confirmed a high robustness of the reaction system and showed carbon monoxide as only byproduct in small ppm concentrations. The gas dosage had a major impact on the catalyst activity. While an oversaturation with carbon dioxide lead to only 14% yield of DMF, a stoichiometric dosage of carbon dioxide to amine lead up to a yield of 43% DMF at an even shorter residence time of 3.5 h. The main reason for this effect could be located on the equilibrium formation of ammonium salts with carbonates and/or carbamates, which reduced the basicity of the reaction system. The whole setup showed a stable activity of over 95 h without catalyst refreshment. Investigations towards the product isolation by distillation showed that all substrate and solvent streams are recyclable and no product decomposition occurred. A ruthenium containing precipitate could be obtained in the purification process that still showed up to 80% of the catalytic activity compared to fresh precursor.</p>	
<p>53. S. Fuchs, M. Steffen, A. Dobrowolski, T. Rösler, L. Johnen, G. Meier, H. Strutz, A. Behr, A. J. Vorholt "Secondary diamines as monomer from bis-hydroaminomethylation of industrial cyclic dienes", <i>Catal. Sci. & Tech.</i>, 2017, 7, 5120-5127 DOI: 10.1039/C7CY01050H</p>	<p>The bifunctional primary amine TCD-diamine (3(4),8(9)-bis(aminomethyl)-tricyclodecane) is accessible by hydroformylation and amination with ammonia of commercially available dicyclopentadiene (dcpd) and offers many applications as a monomer building block. In this work a new simple and selective phosphorous-free and rhodium catalysed bis-hydroaminomethylation (bis-HAM) of non-conjugated diolefins to secondary TCD-di(X)amine monomers for potential new adhesive or coating applications is reported. Key to a successful one phasic bis-HAM is an access of amine and syngas pressure. For the cyclic diene dcpd high conversion combined with very good yields of 94% TCD-di(butyl)amine were achieved under optimised conditions. Transferability to other dienes and primary and secondary amines is effectively shown. This contribution presents for the first time the successful development of an effective application of reactive extraction as a recycling and purification method, to recycle the precious rhodium metal catalyst and separate the diamines. The ex-situ reactive-extraction of the bis-HAM product is conducted using aqueous acetic acid to form water soluble ammonium salt. The resulting ammonium salt is mostly present in the aqueous phase while the rhodium complex maintains in the nonpolar organic phase and is successfully reused in three recycling runs.</p>
	

<p>52. H. Warmeling, D. Janz, M. Peters, A. J. Vorholt, "Acceleration of lean aqueous hydroformylation in an innovative jet loop reactor concept", <i>Chem. Eng. J.</i>, 2017, 330, 585-595 DOI: 10.1016/j.cej.2017.07.152</p>	
<p>The lean biphasic aqueous hydroformylation without chemical additives of the long chain olefin 1-octene using the simple ligand triphenyl trisulfonate sodium salt was investigated in an innovative jet loop reactor on miniplant scale. This elaborate reactor type offers a unique mixing characteristic and is optimised in terms of mechanical energy transfer into the reaction medium through a jet nozzle and organic phase volume fraction. Both variables are important factors in the emulsification of two immiscible liquids. It is subsequently compared to a standard stirred reactor which was also individually optimised. Both concepts showed individual advantages in terms of productivity and catalytic activity. While the jet loop reactor reached high turnover frequencies of 7,640 h⁻¹ the stirred tank reactor showed high space time yields of up to 12.6·10⁻⁵ kmolm⁻³s⁻¹. At very low amounts of dispersed aqueous catalyst phase even very high catalytic activity (TOF=10,960 h⁻¹) was observed in the jet loop reactor. High reactivity could also be preserved in a long time run leading to a total turnover number of 76'500. The jet loop reactor enabled high mass transfer rates for the substrate gases of up to 0.28 s⁻¹ for H₂ and 0.21 s⁻¹ for CO resulting in a mass transfer multiple times faster than the obtained reaction rates. To increase regio-selectivity the bidentate ligand sulfoxanthphos was applied which increased the regio-selectivity up to I:b=53 but with reduced catalytic activity.</p>	


<p>51. M. Furst, V. Korkmaz, T. Gaide, T. Seidensticker, A. Behr and A. J. Vorholt, "Tandem Reductive Hydroformylation of Castor Oil Derived Substrates and Catalyst Recycling by Selective Product Crystallization", <i>ChemCatChem</i>, 2017, 9, 23, 4319 – 4323, DOI: 10.1002/cctc.201700965</p>	
<p>An orthogonal tandem catalytic system consisting of rhodium and ruthenium complexes yields linear C12 a,w-bifunctional compounds from commercial, castor oil derived renewable substrates. With aldehyde yields up to 88% and selectivities to the linear species of up to 95%, this approach is a direct, atom-economic and easy access to potential polymer precursors for polycondensates. Additionally, a straightforward method for selective product crystallisation has been developed, enabling the recycling of the tandem catalytic system for two runs with excellent activity and simultaneously providing a high purity product.</p>	

<p>50. T. A. Faßbach, N. Gösser, F. O. Sommer, A. Behr, X. Guo, S. Romanski, D. Leinweber, A. J. Vorholt, "Palladium-Catalyzed Hydroamination of Farnesene – Long Chain Amines as Building Blocks for Surfactants Based on a Renewable Feedstock", <i>Appl. Catal.</i>, 2017, 543, 173-179 DOI: 10.1016/j.apcata.2017.06.014</p>	
<p>Long chain amines are of great importance for industrial chemistry as they are precursors for surfactants like amine oxides or quaternary ammonia compounds. The atom efficient, homogeneously catalyzed hydroamination using 1,3-dienes offers linear linkage of the amine group to renewables like β-farnesene, offering a C₁₅ skeletal structure, which is a desired size for surfactants, the so called laurics.</p> <p>The presented paper describes the development of a catalytic system for the hydroamination of the industrially available terpene β-farnesene in good to excellent yields. The reaction works with a broad range of amines, aliphatic and aromatic ones. Furthermore, functionalities, like alcohol or ether groups, are tolerated, yielding functionalized farnesylamines. With two model nucleophiles, a scale-up to a 5,000 mL reactor was accomplished; the obtained products were functionalized to surfactants and afterwards characterized by their surface activity.</p>	


<p>49. H. Warmeling, D. Hafki, T. von Söhnen and A. J. Vorholt „Kinetic investigation of lean aqueous hydroformylation – an engineer’s view on homogeneous catalysis” <i>Chem. Eng. J.</i>, 2017, 326, 298–307 DOI: 10.1016/j.cej.2017.05.062</p>	
<p>The additive-free, biphasic aqueous hydroformylation of the long chain olefin 1-octene was investigated with the goal to derive a mathematical expression for the macro kinetic and to increase selectivity towards aldehydes while maintaining fast reaction rates. The influence of different important chemical parameters such as catalyst precursor, catalyst concentration, ligand excess, pH-value, salt concentration, temperature, gas pressure and gas composition was estimated. At 10 MPa and 373 K the highest rate of reaction with 41·10⁻⁵ kmolm⁻³s⁻¹ was reached. An optimal compromise between high selectivity and activity was found at 8 MPa syngas pressure and 353 K reaction temperature. Selectivity was thus increased from 20% to 76% with octene isomers as the only by-products. The rate of reaction was linearly dependent on the created interfacial area as shown in previous publications. The optimised conditions were applied to other olefinic compounds with different structural characteristics. Obtained insights were used to establish a rate expression for this reaction, incorporating the interfacial area between organic substrate and aqueous catalyst phase. This novel approach helps to draw attention towards the aspect of procedural rate enhancement in homogeneous catalysis.</p>	

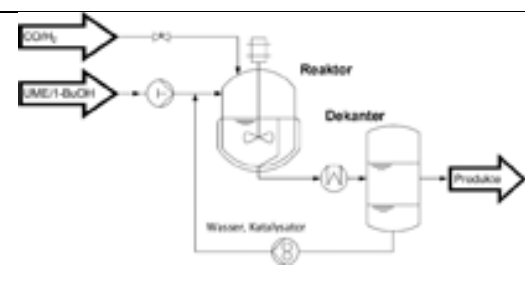
<p>48. T. Gaide, J. Bianga, K. E. Schlipkötter, A. Behr and A. J. Vorholt „Linear selective isomerization / hydroformylation of unsaturated fatty acid methyl esters – A bimetallic approach” <i>ACS Catalysis</i>, 2017, 7 (6), 4163–4171, DOI: 10.1021/acscatal.7b00249</p>	
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A key challenge in synthesis of non-ionic surfactants is opposite polarity of the substrates and the connected challenge to use homogeneous catalysis. We present the telomerisation of β -myrcene with N-methylglucamine to C_{20} -N-alkylated polyols, which show surface activity. The use of aqueous solvent systems along with amphiphilic ligands bridges the polarity gap and shows high reactivities.


<p>47. T. A. Faßbach, F. O. Sommer, A. Behr, S. Romanski, D. Leinweber and A. J. Vorholt „Non-ionic Surfactants from Renewables – Amphiphilic Ligands in Biphasic Reactions”, <i>Catal. Sci. Technol.</i>, 2017, 7, 1650-1653, DOI 10.1039/C7CY00234C Highlighted as cover picture DOI: 10.1039/C7CY90039B</p>	
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A key challenge in synthesis of non-ionic surfactants is opposite polarity of the substrates and the connected challenge to use homogeneous catalysis. We present the telomerisation of β -myrcene with N-methylglucamine to C_{20} -N-alkylated polyols, which show surface activity. The use of aqueous solvent systems along with amphiphilic ligands bridges the polarity gap and shows high reactivities.

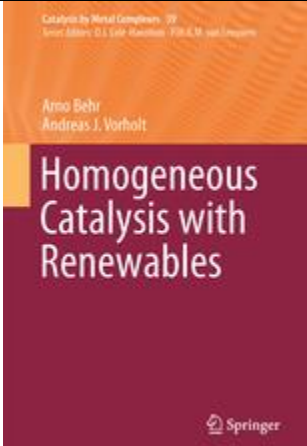
<p>46. T.A. Faßbach, T. Gaide, M. Terhorst, A. Behr, and A. J. Vorholt „Renewable Surfactants via Hydroaminomethylation of Terpenes”, <i>ChemCatChem</i>, 2017, 9, (8) 1359–1362, DOI 10.1002/cctc.201700097 Highlighted as cover picture DOI: 10.1002/cctc.201700553</p>	<p>A catalytic system was developed to enable the use of industrially-available terpenes (myrcene, farnesene) in hydroaminomethylation to obtain renewable building blocks for surfactants in two steps. This homogeneously, tandem-catalyzed reaction includes both a hydroformylation and an enamine condensation, followed by a hydrogenation. Under optimized conditions, the catalytic system ([Rh/dppe]) yields products in high amounts (70%) after short reaction times (3 h), with unprecedentedly high TOFs for the hydroformylation of 1,3-dienes of over 739 [mol·mol⁻¹·h⁻¹]. This is the highest TOF reported to date for a hydroformylation of a 1,3-diene. Furthermore, regioselectivities of 97% and above were observed in the hydroformylation step, which is extraordinarily high for the conversion of 1,3-dienes. The terpene-derived amines obtained were further functionalized to quaternary ammonium compounds, which show surface activity that is quite similar to that of industrially-available quaternary ammonium compounds. The hydroaminomethylation of terpenes achieves higher step-efficiency than industrial means and makes use of an alternative, renewable feedstock to synthesize more environmentally-friendly surfactants.</p>
	

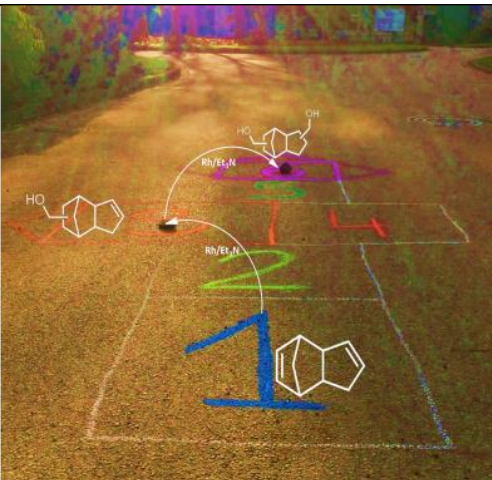
<p>45. J. M. Dreimann, T. A. Faßbach, S. Fuchs, M. R. L. Fürst, T. Gaide, R. Kuhlmann, K. A. Ostrowski, A. Stadler, T. Seidensticker, D. Vogelsang, H. W. F. Warmeling and A. J. Vorholt „Vom Laborkuriosum zum kontinuierlichen Prozess: Die Entwicklung thermomorpher Lösungsmittelsysteme”, <i>CIT</i>, 2017, 252–262, DOI 10.1002/cite.201600119</p>	
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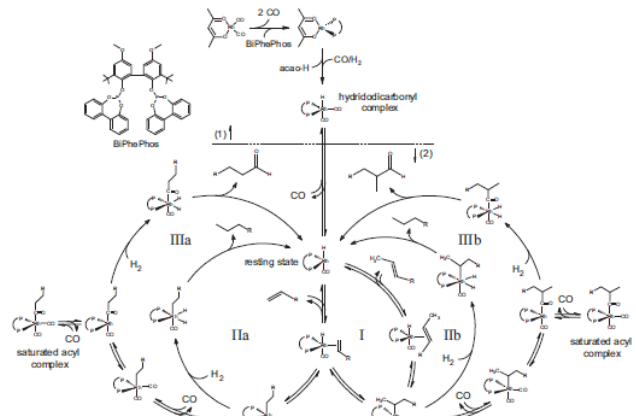
Temperaturgesteuerte Mehrkomponentenlösungsmittelsysteme (TML) sind eine elegante Möglichkeit, homogene Katalysatoren vom Produkt abzutrennen und so zu rezyklieren. Im vorliegenden Beitrag wird die Entwicklung der TML vom Labor- in den kontinuierlichen Miniplant-Maßstab beschrieben und anhand von Beispielen genauer beleuchtet.


<p>44. J. M. Dreimann, F. Hoffmann, M. Skiborowski, A. Behr, and A. J. Vorholt „Merging Thermomorphic Solvent Systems and Organic Solvent Nanofiltration for Hybrid Catalyst Recovery in a Hydroformylation Process”, <i>Ind. Eng. Chem Res.</i>, 2017, 56 (5), 1354–1359, DOI 10.1021/acs.iecr.6b04249</p>	
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The application of homogeneous transition metal catalysts offers various advantages for chemical processes, such as mild reaction conditions and high selectivity. The main drawback is the difficult recovery of these precious catalysts, so that a small loss of catalyst can cause economic insufficiency of a chemical process. Our approach for overcoming this challenge is the application of two different catalyst recovery techniques, which are combined in a so-called hybrid separation process. Here, a thermomorphic solvent system is used for the recovery of the precious rhodium catalyst in a first stage, and a subsequent organic solvent nanofiltration unit is used in a second stage.

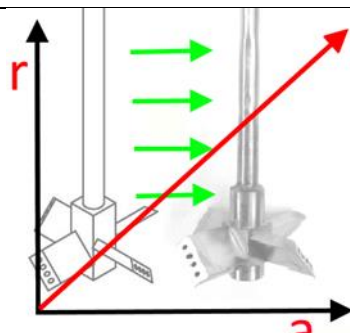
<p>43. A. Behr and A. J. Vorholt Homogeneous Catalysis with renewables, <i>Springer,</i> 2017, DOI: 10.1007/978-3-319-54161-7</p>	
<p>This volume gives a detailed account into how renewables can be transformed into value-added products via homogeneous catalysis, especially via transition metal homogeneous catalysis. The most important catalytic reactions of oleochemicals, isoprenoids, carbohydrates, lignin, proteins and carbon dioxide are described. Special emphasis is placed on carbon-carbon linkage reactions (hydroformylations, dimerisations, telomerisations, metathesis, polymerisations etc.), hydrogenations, oxidations and other important homogeneous reactions (such as isomerisations, hydrosilylations etc.). Also, tandem reactions including isomerising hydroformylations are presented. Wherever possible, the authors have included mechanistic, kinetic, and technical aspects. The reader is therefore given a total overview of the status quo of homogeneous catalysis directed to the most important renewables.</p>	

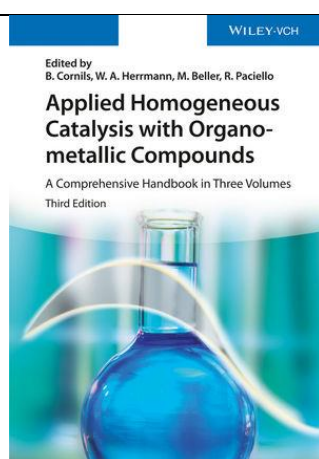
<p>42. S. Fuchs, D. Lichte, M. Dittmar, G. Meier, H. Strutz, A. Behr and A. J. Vorholt „Tertiary amines as ligands in a four-step tandem reaction of hydroformylation and hydrogenation: an alternative route to industrial diol monomers”, <i>ChemCatChem,</i> 2017, 9 (8), 1436–1441 DOI 10.1002/cctc.201601518</p>	
<p>A highly selective synthesis of diols is presented via simple auto-tandem catalysis to connect hydroformylation and hydrogenation reactions by a rhodium-catalyst and tertiary amines as ligands. This system allows the hydroformylation/hydrogenation of non-conjugated cyclic olefins to selectively provide diols under mild reaction conditions. As model substrate, the industrial relevant dicyclopentadiene (dcpd) was chosen. With the reaction system $[\text{Rh}(\text{octanoate})_2]_2$ and triethylamine diols are produced in a high yields of up to 79% with full conversion of intermediate aldehyde or olefin hydrogenation. The scope of the reaction was evaluated and the optimised reaction conditions were successfully scaled up to a 2 L reactor. Finally, the Rh/amine catalyst complex was recycled by a simple water extraction of the diol-product.</p>	

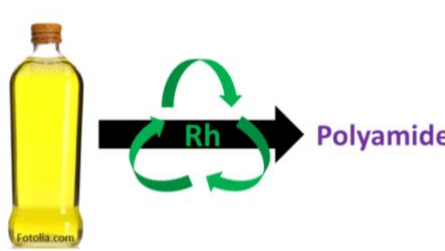
<p>41. A. Jörke, T. Gaide, A. Behr, A. J. Vorholt, A. Seidel-Morgenstern, C. Hamel „Hydroformylation and tandem isomerization–hydroformylation of n-decenes using a rhodium-BiPhePhos catalyst: Kinetic modeling, reaction network analysis and optimal reaction control”, <i>Chem. Eng. J.,</i> 2017, 313, 382-397 DOI 10.1016/j.cej.2016.12.070</p>	
<p>The rhodium-BiPhePhos catalyzed hydroformylation of n-decenes, as representative long-chain olefins, was investigated in this study experimentally and theoretically. Besides hydroformylation activity, the used catalyst enables significant double bond isomerization which is an essential side reaction. Because of this property, highly selective tandem isomerization–hydroformylation reactions that convert mixtures of n-decenes with internal double bond position to the desired terminal aldehyde undecanal are possible using the Rh-BiPhePhos catalyst. Experimentally, a reaction network analysis strategy was applied to study the coupled main and side reactions separately. Subsequently, a mechanistic kinetic model based on an extended Wilkinson-mechanism was developed that includes all relevant main and side reactions. Fitting the model to the 23 well planned experiments was possible with low deviations between model and experiment, including the tandem reaction. It was found that the tandem reaction shows completely opposite dependencies regarding temperature and synthesis gas pressure compared to the conventional hydroformylation of 1-decene, which is also covered by the model. Hence, strategies for optimal reaction performance of the (tandem isomerization-) hydroformylation were developed and presented.</p>	

<p>40. T. Gaide, A. Jörke, K.E. Schlipkötter, C. Hamel, A. Seidel-Morgenstern, A. Behr, A.J. Vorholt, “Isomerization/hydroformylation tandem reaction of a decene isomeric mixture with subsequent catalyst recycling in thermomorphic solvent systems”, <i>Appl. Catal. A.,</i> 2017, 532, 50-56 DOI 10.1016/j.apcata.2016.12.011</p>	
<p>Herein we report about an efficient isomerization/hydroformylation tandem reaction to convert a technical mixture of decene isomers selectively into the linear undecanal in a thermomorphic solvent system. By applying a rhodium/BIPHEPHOS catalyst a high turnover frequency of 375 h^{-1} and high regioselectivity of 92% for the linear product are achieved. Yields up to 70% of the linear aldehyde are obtained. The catalyst can be successfully separated from the product using a thermomorphic solvent system consisting of dimethyl formamide (catalyst phase) and dodecane (product phase). The leaching of the rhodium (0.6% of the initial amount) and phosphorus (1.2% of the initial amount) is very low. The catalyst was successfully recycled five times.</p>	

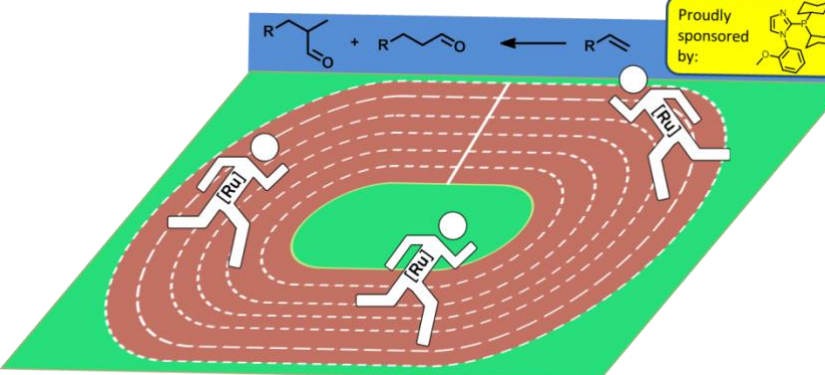
<p>39. A. Behr, D. W. Agar, J. Jörissen and A. J. Vorholt „Einführung in die Technische Chemie“, <i>Springer</i>, 2017, DOI: 10.1007/978-3-662-52856-3</p>	<p>Dieses kompakte Einführungslehrbuch vermittelt die wesentlichen Grundlagen der Technischen Chemie. Es richtet sich in erster Linie an Studierende der Chemie sowie des Chemie- und des Bioingenieurwesens und setzt lediglich Grundkenntnisse in Organischer, Anorganischer und Physikalischer Chemie voraus. Der Stoff ist in vier Teile gegliedert:</p> <ol style="list-style-type: none"> I. Grundlagen: Der Weg von der Laborchemie über den Technikums- bis zum Produktionsmaßstab — Prozessverbund der chemischen Industrie — Produktstammbäume II. Reaktions- und Trenntechnik: Der Reaktionsteil chemischer Prozesse — Ideale und reale Reaktortypen — Thermische und mechanische Grundoperationen — Vorbereitung von Edukten III. Verfahrensentwicklung: Auswahl chemischer Verfahren für die industrielle Chemie — Optimale Rohstoffe — Umweltaspekte — Heterogene Katalyse — Homogene Katalyse — Wirtschaftlichkeit IV. Chemische Prozesse: Wichtigste Produktgruppen der industriellen Chemie — Verarbeitung fossiler Rohstoffe — Organische und anorganische Basis- und Zwischenchemikalien — Endprodukte — Polymere — Organische Feinchemikalien — Nachwachsende Rohstoffe <p>Die aktualisierte zweite Auflage enthält wesentliche Ergänzungen in den Kapiteln zur Katalyse, zur Verarbeitung fossiler Rohstoffe, zur Olefin- und Aromatenchemie, zur Polymerisation und zur Elektrochemie sowie ein gänzlich neues Kapitel zur Wirtschaftlichkeit chemischer Prozesse.</p>
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<p>38. H. Warmeling, R. Koske, A. J. Vorholt „Procedural rate enhancement of lean aqueous hydroformylation of 1-octene without additives“ <i>Chem. Eng. Tech.</i>, 2017, 40, 186-195, DOI: 10.1002/ceat.201600383</p>	
<p>The procedural rate enhancement of a liquid-liquid-gas reaction system by example of the biphasic hydroformylation of 1-octene in miniplant scale is presented. Different stirring techniques were applied on a lean reaction system without the use of chemical additives to increase the internal surface area. Reaction rates were doubled compared to standard laboratory stirring methods (TOF=3250 h⁻¹ to 1650 h⁻¹). While the reaction rate showed a logarithmic relation towards the rate of energy dissipation it was nearly linearly related to the created interfacial area between organic and aqueous phase. Obtained results support the intensively discussed theory that the reaction takes place at the surface. This study also underlines the importance of procedural optimization in multiphase reactions.</p>	


<p>37. A. J. Vorholt, A. Behr „Oleochemistry“ in <i>Applied Homogeneous Catalysis with Organometallic Compounds</i>, Eds Boy Cornils, Wolfgang A. Herrmann, Matthias Beller, Rocco Paciello, 2017, Wiley-VCH DOI: 10.1002/9783527651733.ch34</p>	
<p>Processing renewable resources as a sustainable chemical feedstock has gained more and more attention over the last years. The marketing of sustainable products as well as the oil price volatility make applications of renewables attractive for the chemical industry. The worldwide production of fatty compounds in 2015 amounted around 185 million tons. The main application of fats and oil is the food and feed industry. Nevertheless, up to 15% of the overall amount of fatty materials is converted into technical products, with increasing tendency. The most promising homogeneous catalyzed processes of oleo chemicals to valuable chemical products will be introduced in this chapter.</p>	

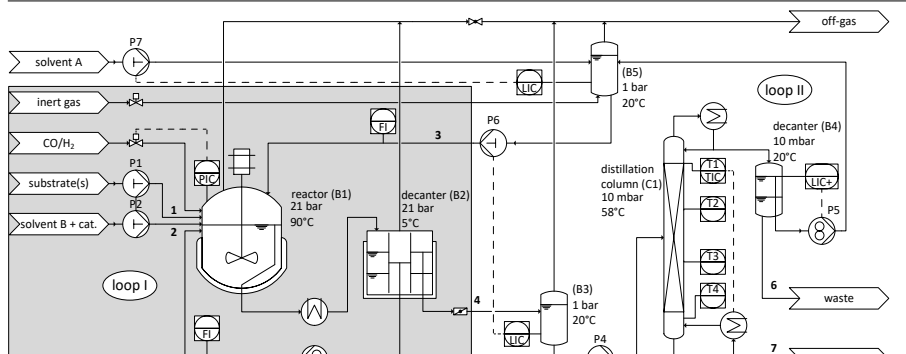
<p>36. A. J. Vorholt, S. Immohr, K.A. Ostrowski, S. Fuchs, A. Behr „Catalyst Recycling in the Hydroaminomethylation of Methyl Oleate: A Route to Novel Polyamide Monomers“, <i>Eur. J. Lipid Sci. Technol.</i>, 2017, 119, (5) 1600211 DOI: 10.1002/ejlt.201600211</p>	
<p>This article describes the development of an effective thermomorphic multicomponent solvent (TMS) system for the production of branched polyamide monomers. In this system, methyl oleate, a renewable from fats & oils, and a functionalised amine are used as starting materials in a tandem catalytic reaction, which merges different reaction steps into a single preparative step. This particular TMS system consisted of a heptane/acetonitrile solvent mixture and made reusing the precious rhodium catalyst possible in three recycle runs. A constant yield of 61 - 65% was obtained for each run due to low catalyst leaching. Fortunately, the catalyst system does not require any additional phosphorous ligands and allows high yields. A scale up for the HAM-product of 11 g in each run was realised. Subsequent hydrogenation of the product directly provided an amine ester, which is a valuable polyamide monomer.</p>	


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<p>35. A. Kämper, P. Kucmierczyk, T. Seidensticker, A. J. Vorholt, R. Franke, A. Behr „Ruthenium-Catalyzed Hydroformylation: From Laboratory to Continuous Miniplant Scale”, <i>Catal. Sci. Technol.</i>, 2016, 6, 8072-8079 DOI 10.1039/C6CY01374K</p>	
<p>Organic solvent nanofiltration is a convenient method for the recovery of homogeneous transition metal catalysts. The long chain olefin 1-dodecene is hydroformylated continuously, while the commercially available catalyst complex is separated efficiently using a commercially available nanofiltration membrane. An advantage of this method is that both reaction and separation take place in a single liquid phase. Only continuous operation shows interactions of reaction and separation in the longrun. Low energy demand, high scalability as well as transferability to other reactions make this method promising for new industrial applications.</p>	

<p>34. J. M. Dreimann, M. Skiborowski, A. Behr, A. J. Vorholt „Recycling homogeneous catalysts simply via organic solvent nanofiltration: New ways to efficient catalysis” <i>ChemCatChem</i>, 2016, 8, 21, 3330-3333, DOI 10.1002/cctc.201601018</p>	
<p>Organic solvent nanofiltration is a convenient method for the recovery of homogeneous transition metal catalysts. The long chain olefin 1-dodecene is hydroformylated continuously, while the commercially available catalyst complex is separated efficiently using a commercially available nanofiltration membrane. An advantage of this method is that both reaction and separation take place in a single liquid phase. Only continuous operation shows interactions of reaction and separation in the longrun. Low energy demand, high scalability as well as transferability to other reactions make this method promising for new industrial applications.</p>	

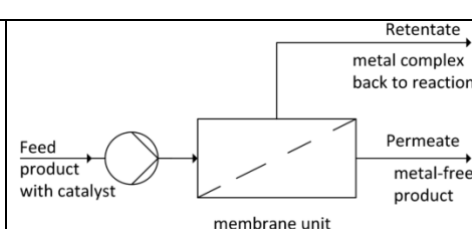
<p>33. T. Seidensticker, H. Busch, C. Diederichs, J. J. von Dincklage, A. J. Vorholt “From Oleo Chemicals to Polymer: Bis-Hydroaminomethylation as a Tool for the Preparation of a Synthetic Polymer from Renewables” <i>ChemCatChem</i>, 2016, 8, 18, 2890-2893, DOI: 10.1002/cctc.201600629</p>	<p>Resource efficient bis-hydroaminomethylation of the castor oil derived renewables methyl 10-undecenoate and 10-undecene 1-ol with piperazine furnished linear, bifunctional molecules. A structured and sustainable path towards a novel polyester from these monomers was developed. Key to success was the selective crystallization of the linear product directly from the crude reaction mixture in >98% purity. Additionally, with this methodology, the homogeneous Rh-catalyst was retained in the supernatant and successfully recycled. Finally, polycondensation yielded a novel piperazine-linked polyester.</p>
	

<p>32. J. M. Dreimann, H. Warmeling, J. N. Weimann, K. Künnemann, A. Behr, A. J. Vorholt “Increasing selectivity of the hydroformylation in a miniplant: catalyst, solvent and olefin recycle in two loops” <i>AIChE J.</i>, 2016, 62, 12, 4377–4383 DOI: 10.1002/aic.15345</p>	<p>The application of thermomorphic solvent systems offers the combination of homogeneous catalysis in a single phase and catalyst recovery via phase separation. To increase economic feasibility the minimization of waste streams and side reactions is desired. For this, a continuous process for the hydroformylation of 1-dodecene in the solvent system DMF/<i>n</i>-decane is shown. While the Rh/Biphephos catalyst is recycled in DMF in a first loop, the <i>n</i>-decane and remaining olefins are separated from the product via distillation to form the second loop. In this process the need for additional solvent supply and the isomerization reaction of 1-dodecene is reduced significantly. The reaction towards internal olefins decreases from initially 15% to 3%. The stable hydroformylation process with a yield of the linear hydroformylation product of 55% and <i>l/b</i>-ratio of 95/5 is shown for 120 h.</p>
	

<p>31. T. Färber, O. Riechert, T. Zeiner, G. Sadowski, A. Behr, A. J. Vorholt “Homogeneously Catalyzed Hydroamination in a Taylor-Couette Reactor using a Thermomorphic Multicomponent Solvent System” <i>Chem. Eng. Res. Des.</i>, 2016, 112, 263–273; DOI: 10.1016/j.cherd.2016.06.022</p>	
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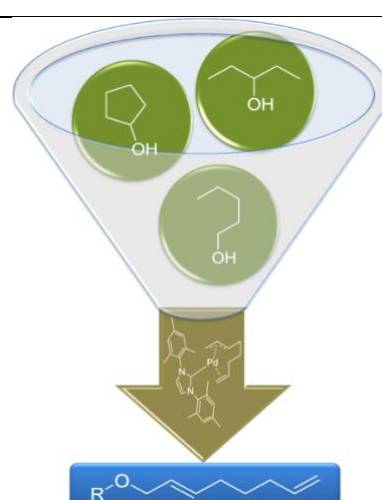
In order to design an innovative continuous process for the conversion of the renewable β -myrcene, three methodical steps are shown in this paper to find a setup for the demanding homogeneously catalyzed hydroamination. First step is the theoretical and practical design of a suitable thermomorphic multicomponent solvent (TMS)-systems for recycling the catalyst system. The necessary phase equilibria were successfully investigated by modelling using the Perturbed Chain – Statistical Associating Fluid Theory (PC-SAFT) and measuring liquid-liquid equilibria of the ternary systems substrates/ solvents mixtures at the separation temperature. In the next step the promising TMS-system was subsequently used to investigate the recycling of the catalyst in continuous operation. A Taylor-Couette reactor (TCR) was developed and modified for the application in homogeneous transition metal catalysis. The reactor was integrated in a miniplant setup and a continuous recycling of the catalyst phase as well as an efficient synthesis of the desired terpenyl amines is achieved in 3 complete cycles. The results show that the TC reactor is suitable for the hydroamination and generates high conversion and yields ($X_{Myr}=82\%$, $Y_{HA}=80\%$). Recycling experiments were conducted successfully in the miniplant setup to show the long-term operation in a period of 24h.

30. J. Dreimann, A. J. Vorholt, M. Skiborowski, A. Behr
“Removal of homogeneous precious metal catalysts via organic solvent nanofiltration”
Chem. Eng. Trans.,
 2016, 47, 343-348; DOI:[10.3303/CET1647058](#)



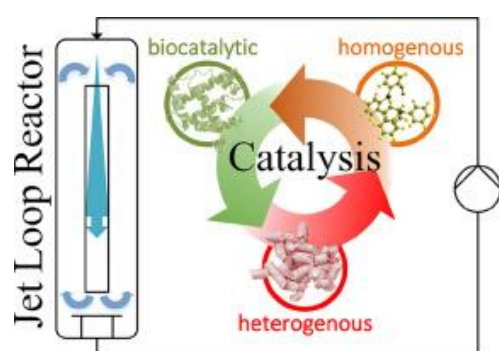
In homogeneous catalysis often precious transition metal complexes are used. Ideally the used catalyst in a specific process is recovered in the downstreaming and recycled back to the reactor. In contrast to the separation of heterogeneous catalysts, the separation of homogeneous catalysts is a crucial issue: Inefficient catalyst recovery and its loss in undesired process streams may even lead to uneconomic processes. The recovery of catalytic species from these streams contributes essentially to the economic efficiency of the production process and prevents the environment from metal contaminations.

29. T. A. Faßbach, R. Kirchmann, A. Behr, S. Romanski, D. Leinweber, A. J. Vorholt
“Telomerization of 1,3-Butadiene with highly substituted Alcohols Using Pd/NHC-Catalysts – Structure-Reactivity-Relationship of the O-Nucleophile”
J. Mol. Catal. A: Chem.
 2016, 423, 526-532
 DOI:[10.1016/j.molcata.2016.05.002](#)



Catalytic telomerization of 1,3-butadiene with alcohols is a catalytic reaction and an effective tool to synthesize 2,7-octadienyl ethers with different characteristics depending on the alcoholic substrate. While Pd/phosphine type catalysts were studied in depth, highly active Pd/NHC catalysts have been studied in the telomerization almost exclusively along with methanol. In the course of employing alcohols from renewables a deeper understanding of the reactivity of these catalysts is needed. In this work we present comprehensive investigations with linear and branched alcohols of different chain-lengths. Distinct tendencies in reaction behavior between primary and secondary alcohols were found and the lower reactivity of secondary alcohols could clearly be attributed to electronic properties, along with steric hindrance. Furthermore, the influence of double bonds in the alcohol chain has been studied. Interestingly, alcohols with double bonds that are not conjugated to the hydroxyl groups were shown to be more active than saturated alcohols. Allylic alcohols however are significantly less reactive than their saturated analog. With the gathered information we were able to deduce a structure-reactivity-relationship of certain functional groups and substitution patterns. These findings were proved by employing terpenols to gain new allylic terpenol ethers.

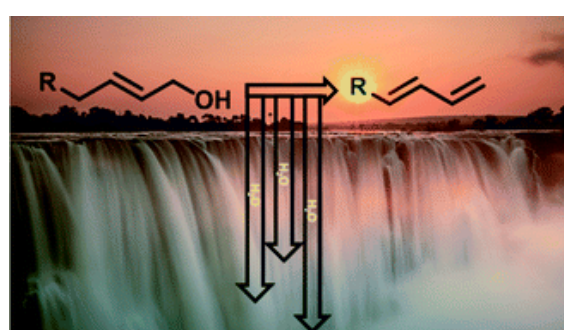
28. H. Warmeling, A. Behr, A. J. Vorholt
“Jet loop reactors as a versatile reactor set up - Intensifying catalytic reactions: A review”
Chem. Eng. Sci.,
 2016, 149, 229–248;
 DOI:[10.1016/j.ces.2016.04.032](#)



Abstract: To overcome the challenges of the increasing global energy and feedstock prices intensified process equipment is one way to develop new efficient production pathways for the chemical industry. In this article the authors convey a thorough overview about the jet loop reactor technique. Ensuing an introduction the operation principle of the reactor type is elucidated. Information available in the literature regarding dimensioning and the physical description is summarized in the following to give an outline of constructional possibilities. To underline the main advantages of the set up the macro and micro mixing properties are discussed in detail and exemplary data is presented. Applied chemical and biochemical reactions are reviewed, with particular focus on the enhancement of catalytic reactions subdivided in homogeneously, heterogeneously and biocatalyzed conversions.

27. K. A. Ostrowski, D. Vogelsang, A. J. Vorholt,
“A general and efficient method for the palladium-catalysed conversion of allylic alcohols into their corresponding dienes”,
Catal. Sci. Technol.,
 2016, 6, 1302-1305; DOI:[10.1039/C5CY02096D](#)

Abstract: A general method was established, converting a broad range of allylic alcohols directly and quantitatively into their corresponding dienes. The developed protocol allows the direct use of allylic alcohols, circumventing the need for their derivatisation into more reactive precursors, thereby minimising waste production with water as the sole co-product.



26. T. Gaide, J. Dreimann, A. Behr, A. J. Vorholt,
“Overcoming Phase-Transfer Limitations in the Conversion of Lipophilic Oleo Compounds in Aqueous Media—A Thermomorphic Approach”,
Angew. Chem. Int. Ed.,
 2016, 55, 2924–2928,
 doi: [10.1002/anie.201510738](https://doi.org/10.1002/anie.201510738)

Abstract: A new process concept has been developed for recycling transition-metal catalysts in the synthesis of moderately polar products via aqueous thermomorphic multicomponent solvent systems. This work focuses on the use of “green” solvents (1-butanol and water) in the hydroformylation of the bio-based substrate methyl 10-undecenoate. Following the successful development of a biphasic reaction system on the laboratory scale, the reaction was transferred to a continuously operated miniplant to demonstrate the robustness of this innovative recycling concept for homogenous catalysts.

25. T. Seidensticker, J. M. Vosberg, K. A. Ostrowski, A. J. Vorholt,
“Rhodium-Catalyzed Bis-Hydroaminomethylation of Linear Aliphatic Alkenes with Piperazine”,
Adv. Synth. Catal.,
 2016, 358, 610–621,
 DOI: [10.1002/adsc.201500896](https://doi.org/10.1002/adsc.201500896)

Abstract: An efficient protocol was developed to prepare a series of dialkylpiperazines *via* Rh-catalyzed *bis*-hydroaminomethylation of linear aliphatic alkenes with piperazine. The well-known Rh/Biphephos catalytic system was applied, yielding the desired dialkylpiperazines within six tandem catalytic steps, already at low catalyst loadings of 0.1 mol%. For the model alkene 1-octene, good yields and linearities of 80% and 77:23, respectively, were achieved under optimized conditions. Influences on the catalytic system regarding *n/iso* ratio, possible side reactions and the reaction path are discussed on the basis of yield vs. time plots and parameter optimization. With the developed general protocol, other linear, functionalized and branched substrates were effectively transformed to the corresponding linear *N,N*-disubstituted piperazines.

24. K. A. Ostrowski, D. Vogelsang, T. Seidensticker, A. J. Vorholt,
“Direct Synthesis of an α,ω -Diester from 2,7-Octadienol as Bulk Feedstock in Three Tandem Catalytic Steps”
Chem. Eur. J.
 2016, 22, 1840-1846. DOI:
[10.1002/chem.201503785](https://doi.org/10.1002/chem.201503785)

Abstract: Good things come in threes: A new auto-tandem catalytic process enables direct access to C_{10} α,ω -diesters from 2,7-octadienol by merging three different reactions in sequence: ether formation, ether carbonylation and alkoxy carbonylation. Good yields of the desired diester are obtained with a Pd/Xantphos catalyst complex. The application of other ligands leads to different reaction pathways and products.

23. T. Seidensticker, D. Möller, A. J. Vorholt,
“Merger of Johnson–Claisen rearrangement and alkoxy carbonylation for atom efficient diester synthesis”
Tetrahedron Lett.,
 2016, 57, 371-374. DOI:
[10.1016/j.tetlet.2015.12.032](https://doi.org/10.1016/j.tetlet.2015.12.032)

Abstract: The orthoester Johnson–Claisen rearrangement of allyl alcohol with triethyl orthoacetate for the synthesis of ethyl 4-pentenoate has been optimized, in order to allow for a selective and efficient subsequent alkoxy carbonylation using formates in an atom efficient manner. Diethyl adipate was successfully yielded in up to 89% applying very low orthoester excess, formic acid and mild reaction conditions in an innovative, one-pot procedure.

22. K. A. Ostrowski, D. Lichte, M. Stuck, A. J. Vorholt,
“A comprehensive investigation and optimisation on the proteinogenic amino acid catalysed homo aldol condensation”
Tetrahedron,
 2016, 72, 592-598. DOI:
[10.1016/j.tet.2015.11.069](https://doi.org/10.1016/j.tet.2015.11.069)

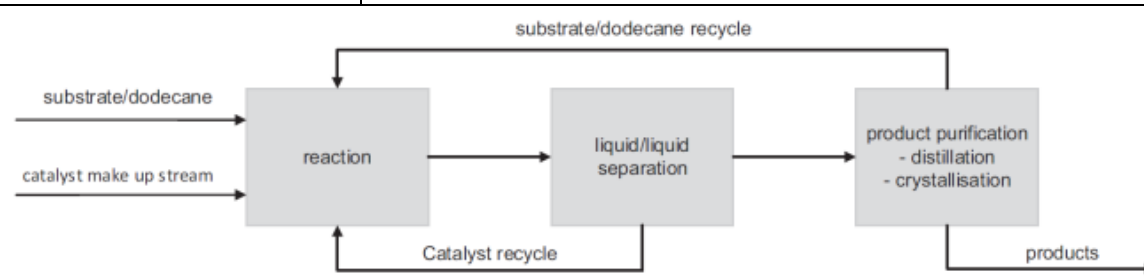
Abstract: Twenty proteinogenic amino acids were applied as organocatalysts in the homo aldol condensation of aldehydes. Basic amino acids were highly active at low catalyst concentrations and aromatic amino acids generated very good yields in short reaction times. The side-chain groups have no catalytic activity, but they have a big impact on the catalytic activity. A general method was developed, being transferable to other substrates.

<p>21. T. Gaide, A. Behr, M. Terhorst, A. Arns, F. Benski, A. J. Vorholt, "Katalysatorvergleich bei der Hydroesterifizierung von 10-Undecensäuremethylester in thermomorphen Lösungsmittelsystemen", <i>CIT</i>, 2016, 88, 158-167. DOI: 10.1002/cite.201500096</p>	<p>Abstract: Two homogeneous palladium catalysts for the hydroesterification of methyl 10-undecenoate to dimethyl dodecanedioate are compared. The reaction rates of both catalysts were tested in thermomorphic solvent systems and the reaction conditions were optimized. Afterwards the separation of catalyst and product was investigated and the applicability of thermomorphic solvent systems was validated via catalyst recycling experiments.</p>

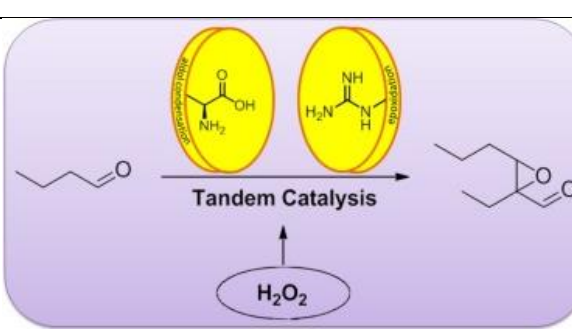
<p>20. T. Seidensticker, A. J. Vorholt, A. Behr, "The mission of addition and fission – catalytic functionalization of oleochemicals", <i>Eur. J. Lipid Sci. Technol.</i> 2016, 118, 3-25. DOI: 10.1002/ejlt.201500190</p>	<p>Abstract: Oleochemicals are used in the chemical industry in numerous processes and applications, having the largest share among all other renewable resources. Besides the well-known transformations performed at the carboxylic moiety of the alkyl chain, many natural occurring fatty compounds offer a further opportunity for refinement, that is: catalytic functionalization of the C=C double bond. In the present review, the authors describe the mission of the scientific work that is performed at the chair of Technical Chemistry at the TU Dortmund towards selective and atom economic functionalization of oleochemicals. Special emphasis lays on homogenous transition metal catalysis towards potential applications of the resulting products and their continuous production in miniplant scale. The given examples are discussed in the context of the work of other groups and summarize recent developments in the field of addition and fission reactions of oleochemicals.</p>

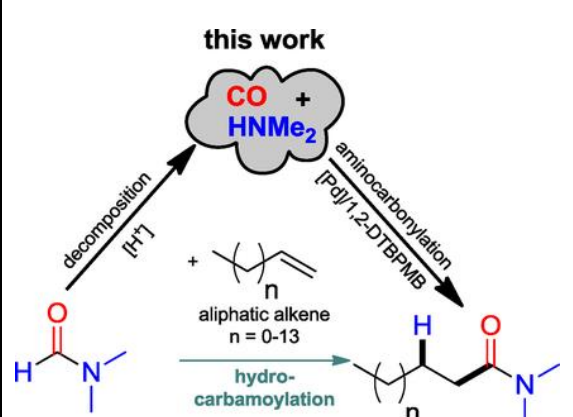
<p>19. J. Dreimann, P. Lutze, M. Zagajewski, A. Behr, A. Górak, A. J. Vorholt, "Chemical Engineering and Processing, Highly Integrated Reactor-Separator Systems for the Recycling of Homogeneous Catalysts" <i>Chem. Eng. Proc.</i> 2016, 99, 124-131. DOI: 10.1016/j.cep.2015.07.019</p>	<p>Abstract: Homogeneous transition metal catalysts allow highly selective conversion of reactants at mild reaction conditions. Main drawback of this catalytic method is a difficult recovery of the catalyst, dissolved in the reaction phase. One recovery method is the decrease of the temperature in the reaction phase in order to generate two phases in which the product and the catalyst show different solubilities. This is known as thermomorphic multicomponent solvent (TMS) system. Another method to separate the catalyst directly from the reaction phase is the application of the organic solvent nanofiltration (OSN). For both recovery methods proper operating windows of reaction and separation are necessary to reach a high selectivity and yield in the reaction on one hand and prevent catalyst loss through efficient separation on the other. Only the combination of suitable solvents, reaction conditions and separation methods guarantee a successful performance of the whole catalytic system.</p>

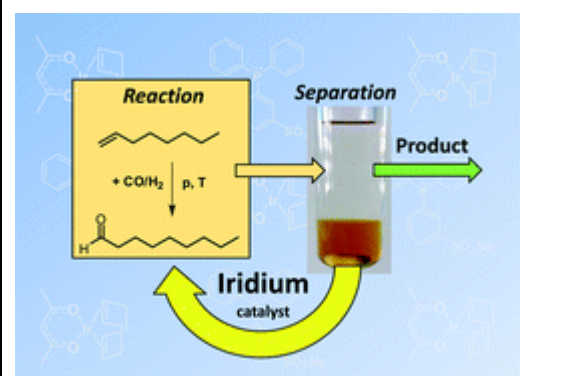
<p>18. K. McBride, T. Gaide, A. J. Vorholt, A. Behr, K. Sundmacher, "Chemical Engineering and Processing, Thermomorphic Solvent Selection for Homogeneous Catalyst Recovery based on COSMO-RS", <i>Chem. Eng. Proc.</i> 2016, 99, 97-106. DOI: 10.1016/j.cep.2015.07.004</p>	<p>Abstract: One method that has shown much promise due to its simplicity and effectiveness in homogeneous catalyst recovery is the use of thermomorphic solvent systems (TMS). In this contribution, a novel method for TMS solvent selection based on quantum chemical predictions of catalyst solubility and phase equilibrium is presented. This allows for solvent effects on the catalyst to be incorporated directly into the solvent screening process. A framework for TMS design is developed and implemented using the hydroformylation of 1-dodecene and the rhodium-Biphephos catalyst as an example reaction system. In this way, several promising TMS systems were identified. Experiments were then performed to validate the model based on catalyst partitioning and phase equilibrium. This was followed by conducting a series of reactions to investigate feasibility of the new TMS systems in the actual hydroformylation. In the end it was shown that although some problems arise from inconsistencies in phase equilibrium predictions, the method does provide a functioning <i>a priori</i> basis for TMS development.</p>

<p>17. T. Gaide, A. Behr, A. Arns, F. Benski, A. J. Vorholt, "Hydroesterification of methyl 10-undecenoate in thermomorphic multicomponent solvent systems—Process development for the synthesis of sustainable polymer precursors", <i>Chem. Eng. Proc.</i>, 2016, 99, 197-204. DOI: 10.1016/j.cep.2015.07.009</p>	<p>Abstract: In this paper, we present a process concept for the atom economic hydroesterification of renewable methyl 10-undecenoate in thermomorphic multicomponent solvent (TMS) systems. Resulting dimethyl dodecanedioate is a polymer building block used e.g. in Nylon 6,12. As a suitable recycling technique a thermomorphic multicomponent solvent system consisting of methanol and dodecane is employed to recycle the palladium/1,2-bis(di-tert-butylphosphino)methyl)benzene/methanesulfonic acid catalyst. Product yields up to 79% and a high regioselectivity of 94% to the linear product are obtained. Low leaching of the catalyst into the product phase with 1% in respect of palladium and phosphorous is observed. Robustness and stability of the catalyst is shown in eight recycling runs without any loss of selectivity in the reaction.</p>
	

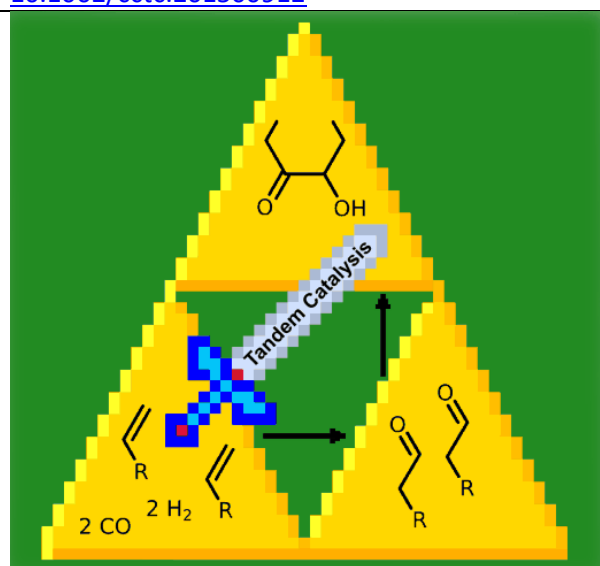
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<p>16. K. A. Ostrowski, D. Lichte, M. Terhorst, A. J. Vorholt, "Two sides of the same amino acid—development of a tandem aldol condensation/epoxidation by using the synergy of different catalytic centres in amino acids", <i>Appl. Catal. A</i>, 2015, 509, 1–7. DOI: 10.1016/j.apcata.2015.10.018</p>	
<p>Abstract: 20 proteinogenic amino acids were applied as organocatalysts in the epoxidation of α-branched, α,β-unsaturated aldehydes. The most active amino acids were used as organocatalysts in the development of a new tandem catalysis consisting of a homo aldol condensation and epoxidation, wherein the α-amino group is catalysing the aldol condensation and the side chain group is catalysing the epoxidation. Excellent selectivities and very good yields were obtained by converting the aldehyde directly into the epoxy aldehyde within this tandem catalysis</p>	

<p>15. T. Seidensticker, M. R. L. Furst, R. Frauenlob, J. Vondran, E. Paetzold, U. Kragl, A. J. Vorholt, "Palladium-Catalyzed Aminocarbonylation of Aliphatic Alkenes with <i>N,N</i>-Dimethylformamide as an In Situ Source of CO", <i>ChemCatChem</i>, 2015, 7, 4085-4090. DOI: 10.1002/cctc.201500824</p>	<p>Abstract: The palladium-catalyzed aminocarbonylation of aliphatic alkenes is presented for the first time without the need for external CO pressure. <i>N,N</i>-dimethylformamide (DMF) is used as an in situ source of both the required carbon monoxide and the amine substrate. The applied palladium catalytic system is well-known for a number of carbonylation reactions, including those with CO surrogates and tandem isomerizing carbonylations. The reaction pathway was investigated and proved to proceed by an acid-catalyzed DMF decomposition to CO and dimethyl amine with subsequent aminocarbonylation of the alkene. Pressure-versus-time curves gave more insight into the correlation between acid concentration and aminocarbonylation activity. Aliphatic alkenes (terminal and internal) are transformed, also in commercial glassware, into the corresponding linear <i>N,N</i>-dimethylamides with excellent selectivities. Hence, amide synthesis by aminocarbonylation moves closer to application in standard organic laboratories.</p>
	

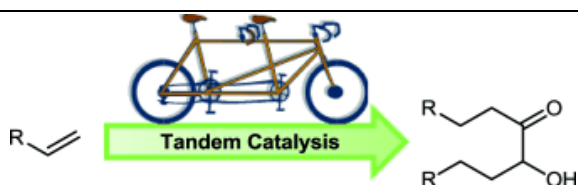
<p>14. A. Behr, A. Kämper, R. Kuhlmann, A. J. Vorholt, R. Franke, „First efficient catalyst recycling for the iridium-catalysed hydroformylation of 1-octene“, <i>Catal. Sci. & Technol.</i> 2015, 6, 208-214. DOI: 10.1039/C5CY01018G</p>	<p>Abstract: This paper describes the development of an efficient catalyst recycling concept for the iridium-catalysed hydroformylation of 1-octene through the investigation of biphasic systems, thermomorphic solvent systems and an <i>ex situ</i> extraction. Particularly high selectivities (>90%) towards the desired aldehydes as well as low rates of iridium leaching were observed using the monosulfonated triphenylphosphine ligand (TPPMS). In polar solvents such as propylene carbonate or <i>N,N</i>-dimethylformamide, low rates of catalyst leaching (0.2%) as well as high rates of product separation (nearly 80%) were achieved. High reaction rates and a long-term activity and stability of the catalyst were observed using the solvent <i>N,N</i>-dimethylformamide and the extraction with non-polar solvents</p>
	

13. K. A. Ostrowski, T. A. Faßbach, D. Vogelsang, A. J. Vorholt,
“The Quest for Decreasing Side Products and Increasing Selectivity in Tandem Hydroformylation/Acyloin Reaction”
ChemCatChem
 2015, 7, 2607-2613. DOI:
[10.1002/cctc.201500727](https://doi.org/10.1002/cctc.201500727)
 Highlighted as cover picture DOI:
[10.1002/cctc.201500912](https://doi.org/10.1002/cctc.201500912)



Abstract: A highly selective catalyst system was developed for the recently discovered tandem hydroformylation/acyloin reaction by systematic investigations and changes of reaction conditions. This new catalyst system is characterized by an excellent selectivity of the desired reaction pathway with negligible amounts of side products. A successful application of the tandem hydroformylation/acyloin reaction to a variety of olefins is enabled with comparable excellent selectivities up to >99% for the first and second reaction step, therefore a general synthesis for the conversion of olefins into acyloins is found. Furthermore, very good to excellent yields for the intermediates and final acyloin products were observed within two catalysed reactions in one preparative step. The acyloin product was applied as a nonpolar precursor for surfactants. After attaching a polar head group to the acyloin and determination of tensiometric data, the molecule showed industrial relevant surface-active properties.

12. K. A. Ostrowski, T. A. Faßbach, A. J. Vorholt,
„Tandem Hydroformylation/Acyloin Reaction – The Synergy of Metal Catalysis and Organocatalysis Yielding Acyloins Directly from Olefins”,
Adv. Synth. Catal.
 2015, 357, 1374–1380.
 DOI:[10.1002/adsc.201401031](https://doi.org/10.1002/adsc.201401031)



Abstract: A novel, atom efficient, orthogonal tandem catalysis was developed yielding acyloin products (α -hydroxy ketones) directly from olefins under hydroformylation conditions. The combination of a metal-catalysed hydroformylation and an organocatalysed acyloin reaction provides three atom efficient C-C bond formations to linear, multifunctional molecules via linkage of the intermediate *n*-aldehydes. Additionally, the rhodium catalyst system gives a high *n/bra* ratio with an exclusive conversion of the terminal double bond in the hydroformylation and the *n*-aldehydes are converted selectively to their acyloins.

11. A. Behr, A. J. Vorholt, T. Seidensticker,
„An Old Friend in a New Guise-Recent Trends in Homogeneous Transition Metal Catalysis”
ChemBioEng Rev.
 2015, 2, 6-21. DOI:[10.1002/cben.201400034](https://doi.org/10.1002/cben.201400034)

Abstract: The present contribution surveys recent developments and trends in homogeneous transition metal catalysis (HTMC). Emphasis is on industrially relevant reactions, such as hydroformylations, carbonylations, hydrogenations, oxidations, aminations, metatheses, and related tandem reactions. Besides classical petrochemical feedstocks, transformations of renewable resources are also taken into account. Additionally, examples of homogeneous catalysis in continuously operated miniplants are disclosed.



2014

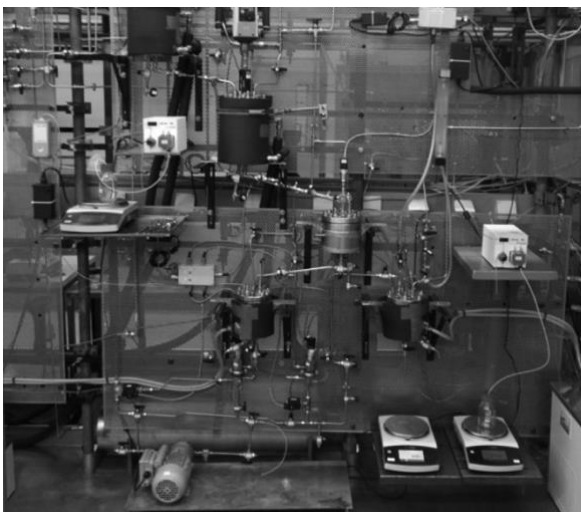
10. A. Behr, A. J. Vorholt, K. A. Ostrowski, T. Seidensticker,
„Towards resource efficient chemistry: tandem reactions with renewables”,
Green Chem.
 2014, 16, 982-1006, DOI:[10.1039/C3GC41960F](https://doi.org/10.1039/C3GC41960F).

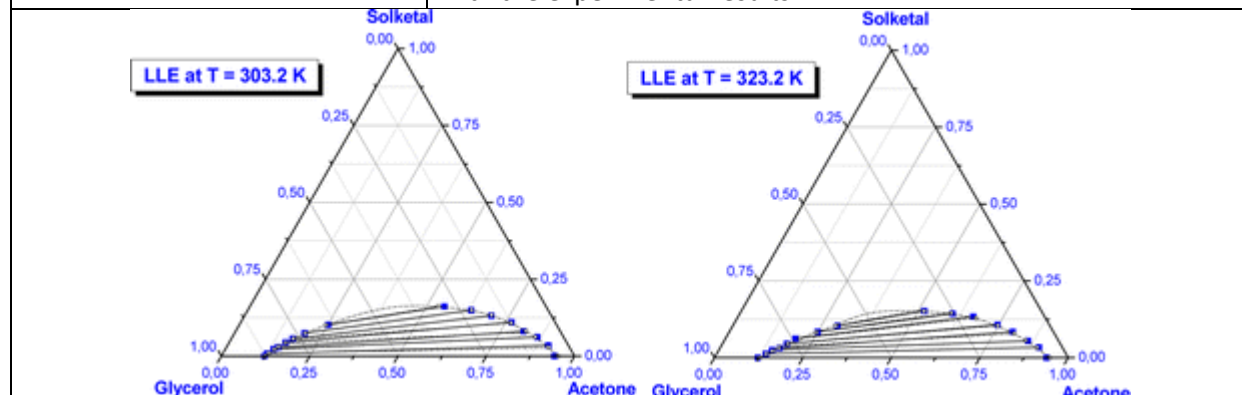



Abstract: In an economically expanding world new sustainable concepts have to be developed in order to overcome growing problems of resource availability. Merging different “Green principles” is a promising concept in this respect, e.g. the combination of tandem reactions and renewables. This review summarizes the trends in this field and demonstrates advantages and future demands. Four reactions, namely metathesis, hydroformylation, defunctionalisation and isomerisation, have been identified for transforming renewables in tandem reactions. Every reaction yields a reactive intermediate or secures a tailored selectivity in order to use the natural molecular structure of renewables.

9. A. Behr, A. J. Vorholt,
„Neue Trends in der homogenen Übergangsmetallkatalyse”,
CIT,
 2014, 86, 2089–2104,
 DOI: [10.1002/cite.201400109](https://doi.org/10.1002/cite.201400109)

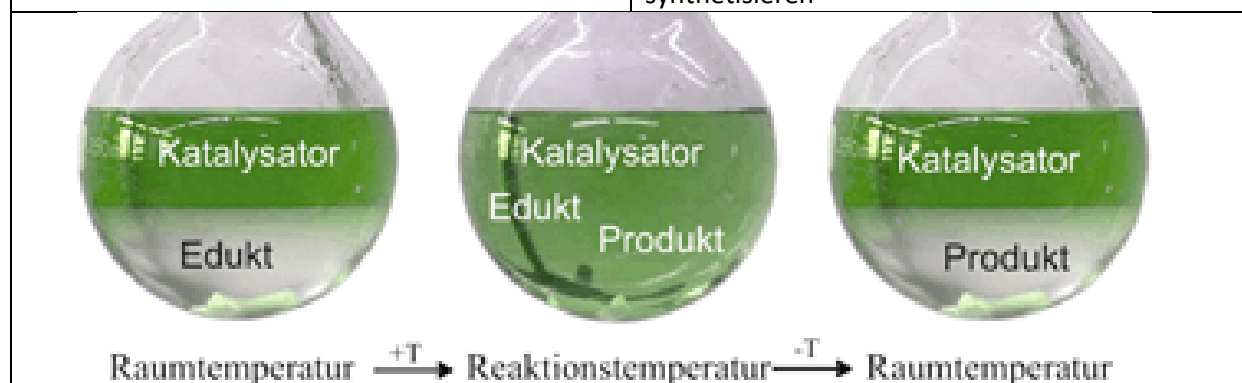
Abstract: This contribution presents an overview of current developments in homogeneous catalysis. In this respect, the focus lies on industrial relevant reactions like hydroformylation, carbonylation, hydrogenation, oxidation, amination and metathesis and resulting tandem reactions. Beyond the classical petrochemical feedstocks, also renewables such as a sustainable feedstock are discussed. Selected examples of homogeneous catalysis in continuously operated miniplants are given.

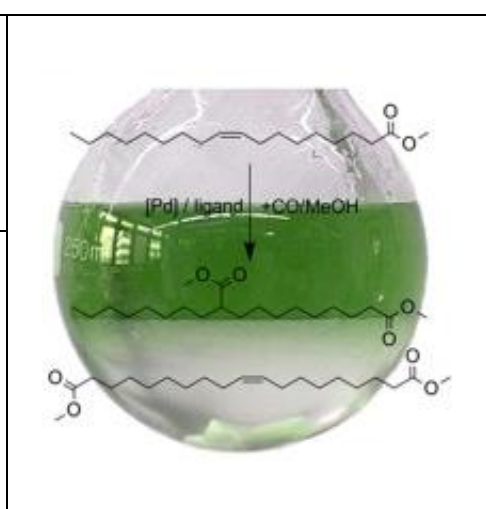


<p>8. J. Esteban, A. J. Vorholt, A. Behr, M. Ladero, F. Garcia-Ochoa, “Liquid-liquid equilibria for the system acetone + solketal + glycerol”, <i>J. Chem. Eng. Data</i> 2014, 59, 2850-2855, DOI:10.1021/je500469a</p>	<p>Abstract: Experimental measurements of the liquid–liquid equilibrium of the ternary system consisting of acetone + solketal + glycerol were made. The conditions selected for this study were (303.2, 313.2, and 323.2) K at 101.3 kPa, relevant for the synthesis of solketal from glycerol and acetone through a ketalization reaction. The data obtained were correlated to the nonrandom two liquid (NRTL) model, and the binary interaction parameters of the ternary system were retrieved after the optimization of the nonrandomness binary interaction parameters. The liquid–liquid equilibrium data predicted by the NRTL model agreed adequately with the experimental results.</p>
	


<p>7. A. Behr, T. Seidensticker, A. J. Vorholt, “Diester monomers from methyl oleate and proline via tandem hydroaminomethylation-esterification sequence with homogeneous catalyst recycling using TMS-technique”, <i>Eur. J. Lipid Sci. Technol.</i> 2014, 166, 477-485, DOI: 10.1002/ejlt.201300224</p>	<p>Abstract: Diesters from renewables are attractive precursors in various polymer applications. In this regard, unsaturated fatty compounds such as methyl oleate are interesting starting materials as it is possible to introduce different functional groups by modifying the double bonds and due to the existing carboxylic moiety. Another interesting class of renewables are amino acids, such as L-proline, which provide naturally occurring amino and carboxylic moieties. Combining these two renewables in one reaction sequence consisting of hydroformylation, condensation, hydrogenation (i.e., hydroaminomethylation; HAM) and esterification results in interesting biopolymer-precursors. In this paper, we present a combination of these four reactions used to functionalize methyl oleate to produce diesters in one pot. These diesters were successfully separated from the catalyst using thermomorphic solvent systems (TMS)-technique, resulting in minimal leaching of the precious metal rhodium into the product phase. Catalyst recycling was shown for three recycling runs in which the catalyst activity was maintained.</p>
	

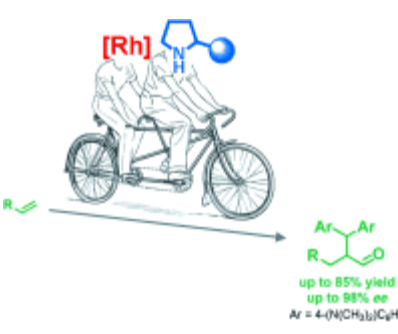
2013

<p>6. A. J. Vorholt, P. Neubert, A. Behr, „Katalytische Funktionalisierungen von Oleylalkohol in thermomorphen Lösungsmittelsystemen zur Synthese potenzieller Biotenside und -Monomere“, <i>CIT</i> 2013, 85, 1540-1547, DOI:10.1002/cite.201300049</p>	<p>Abstract: Zwei Funktionalisierungen des Fettalkohols Oleylalkohol mithilfe von Kohlenmonoxid werden vorgestellt. Durch die beiden homogen katalysierten Reaktionen Hydroaminomethylierung und Hydroesterifizierung ist es möglich ausgehend von ungesättigten Fettalkoholen neuartige Tenside oder Monomere für Polyester zu synthetisieren</p>
	


<p>5. A. Behr, A.J. Vorholt, N. Rentmeister, “Recyclable homogeneous catalyst for the hydroesterification of methyl oleate in thermomorphic solvent systems”, <i>Chem. Eng. Sci.</i> 2013, 99, 38-43 DOI: 10.1016/j.ces.2013.05.040</p>	
<p>Abstract: Easy assessible renewable Diesters: Hydroesterification of the renewable methyl oleate leads to branched and linear diesters. A catalyst system from XANTphos and palladium governs the selectivity for the products by simple variation of reaction parameters. Thermomorphic solvent system technique is used for a catalyst separation. The catalyst can be recovered and reused for a number of cycles with negligible loss in activity.</p>	

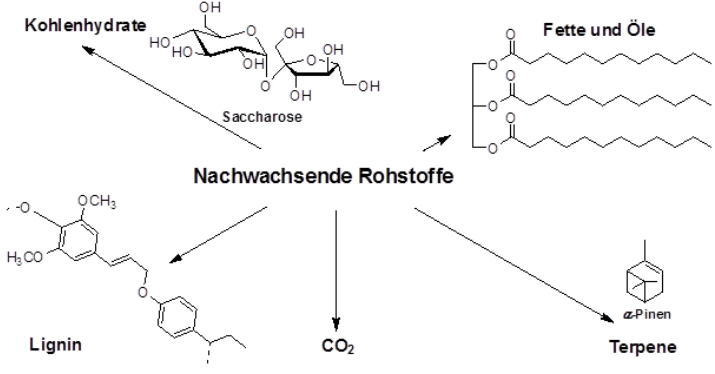
2012

<p>4. A. Behr, A. J. Vorholt, “Hydroformylation and Related Reactions of Renewables Resources” <i>Top. Organomet. Chem.</i> 2012 39, 103-128, DOI: 10.1007/978-3-642-28288-1_3</p>	<p>Abstract: Today, the increasing global population and the rising consumption of fossil resources for energy and material use are important issues for research activities in the field of transformation of renewable resources. In petrochemistry, well-established reactions like hydroformylation are performed in multiton plants all over the world and are important examples for processing new resources beyond fossil feedstocks. This chapter deals with the application of three important reactions with carbon monoxide, specifically hydroformylation, hydroaminomethylation, and hydroesterification with renewables which have a C–C-double bond in the starting material. In these reactions, unsaturated oleocompounds and a variety of terpenes can be employed because of their naturally available double bonds.</p>
	

<p>3. J. Stiller, A. J. Vorholt, K. A. Ostrowski, A. Behr, M. Christmann, „Enantioselective Tandem Reactions at Elevated Temperatures: One-Pot Hydroformylation/SN1 Alkylation”, <i>Chem. Eur. J.</i> 2012, 18, 9496–9499, DOI:10.1002/chem.201200639 Highlighted in <i>Synfacts</i>, 2012, 8, 1094 DOI: 10.1055/s-0032-1317302</p>	
<p>Abstract: Canned heat: The optimization of a tandem sequence of a metal-catalyzed and a subsequent organocatalytic reaction is described (see figure). The tandem sequence was initially optimized toward a high yield by variations of substrate ratio, rhodium precursor, and ligands. The tandem reaction is also extendable to more complex alkenes and to substrates with additional functional groups.</p>	

Prior 2011

<p>2. A. Behr, L. Johnen, A. J. Vorholt, „Telomerization of Myrcene and Catalyst Separation by Thermomorphic Solvent Systems”, <i>ChemCatChem</i> 2010, 2, 1271 – 1277, DOI:10.1002/cctc.201000116</p>	
<p>Abstract: Telomerization of common petrochemical 1,3-dienes such as butadiene and isoprene have long been successful with different nucleophiles; however, the telomerization of the C₁₀ hydrocarbon myrcene was not known until now. Herein, the first telomerization of the monoterpene myrcene with diethylamine is discussed, which provides an atom-economical way of generating C₂₀ amines in a single step. Variation of the palladium precursors and phosphorous ligands and optimization of solvent and additives led to the optimum catalyst system [Pd(MeCN)₄](BF₄)₂/PPh₃. By using a thermomorphic solvent system, the Pd complex can be easily separated with low leaching values.</p>	

<p>1. A. Behr, A. J. Vorholt, L. Johnen, „Aus der Natur für die Chemie”, <i>Nach. Chem.</i> 2009, 57, 757-76, DOI: 10.1002/nadc.200966112</p>	
<p>Abstract: Mit nachwachsenden Rohstoffen lassen sich neue Produkte synthetisieren oder bei bekannten Produkten fossile Rohstoffe ersetzen. Die Katalyse macht viele Produktionswege erst möglich.</p>	