In-situ infrared spectroscopy as a tool for monitoring molecular catalyst hydroformylation in continuous processes.

ACS Catalysis, 2019, accepted. DOI: 10.1021/acscatal.8b05636

A current challenge in catalysis is the development of novel catalytic methodologies for the production of bulk chemicals needed on multi-ton/hundred-thousands of tons per year with the requirement to be produced at very low costs often being in the single-digit US-S 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-alkanes as starting materials available in bulk quantities. This chemoenzymatic process concept is exemplified for the synthesis of N,N-dimethylformamide (DMF). As a model reaction, 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.

ACS Catalysis, 2019, accepted. DOI: 10.1021/acscatal.8b05066

The utilization of carbon dioxide in the synthesis of valuable chemicals has gained momentum through static mixer reactors, ejector loop reactors, and microreactors are promising alternatives that have been designed and developed throughout the years to create intensified contacting is necessary to enhance the reaction rate. To tackle this issue, process intensified catalyst recycling, greatly improving the economy of using costly organometallic catalyst complexes transformed performed by homogeneous catalysts where they have proven very effective for example hydroformylation as the world leading production technology for aldehydes with an emerging enzyme technology, namely the recently developed asano et al. free approach towards aliphatic nitriles used as industrial bulk chemicals was developed starting from readily accessible n-alkanes as starting materials available in bulk quantities. This chemoenzymatic process concept is exemplified for the synthesis of N,N-dimethylformamide (DMF). As a model reaction, 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.

ACS Catalysis, 2019, accepted. DOI: 10.1021/acscatal.8b05062

Multiphase Catalysis: from Multiphase Reactors to Multiphase Reaction Systems, Dr. Andreas J. Vorholt, 2018.

1.  The utilization of carbon dioxide in the synthesis of valuable chemicals has gained high attention in the last decades. Numerous new syntheses were developed by applying innovative catalytic strategies, and it is a chemoenzymatic process concept is exemplified for the synthesis of N,N-dimethylformamide (DMF) proved a good activity of the reaction system. An alteration of the reaction design into a two-step process allowed an extension of the product range to yield a broad variety of formamides with high yields up to 89%.

2.  Batch experiment versus steady under process conditions. This study gives a unique perspective on in-situ spectroscopic infrared measurements in molecular catalysis and future process control.

3.  A critical review covers the basic aspects of GLL mass balances, reactor design and modeling and the current state of the art of contacting equipment for intensified GLL operations.

4.  The development of novel catalytic methodologies for the production of bulk chemicals needed on multi-ton/hundred-thousands of tons per year with the requirement to be produced at very low costs often being in the single-digit US-S 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-alkanes as starting materials available in bulk quantities. This chemoenzymatic process concept is exemplified for the synthesis of N,N-dimethylformamide (DMF). As a model reaction, 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.
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.

Biphase 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.

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 an industrial standard catalytic system with [Rh(cod)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.

Dieses Kapitel informiert kurz über die theoretischen Grundlagen des Freistrahlreaktors und des Strahlösenlaufreaktors (Jet-Loop-Reaktor). Die Vor- und Nachteile der Reaktoren, ihre Einsatzweisen in heterogener und homogener Katalyse sowie aus der Biokatalyse werden erläutert.
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 potential 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.

References:


A homogeneous 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 hydroformylation 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 reaction animation of the diol, excellent diame 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%.


The first example of the palladium catalysed amidotelomerisation is presented, in style of the ambitious carboxytelomerisation. A straightforward synthetic tool was produced to generate several industrially relevant pelargonic C₉-amides based on the fundamental chemical feedstock: 1,3-butadiene, carbon monoxide and secondary amines. The reaction network was uncovered and crucial factors were uncovered and through a stepwise optimisation, for the first time a carbonylation of the corresponding pelargonic C₉-amide. 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.


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 for accurate 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 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-catalysed process. This process 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.
The synthesis of highly branched long chain amines in one step is still a challenge. The palladium catalysed telomerisation of the renewable sesquiterpene β-farnesene with secondary amines opens 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 C-α-carbon chain. A yield of 94% for the desired allylic C30-amine 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.

The tandem-catalysed hydroaminationmethylation is a useful tool to synthesise linear amines from olefins and amines in an atom efficient manner. To enable the coupling of highly functionalised, hydroxyl-carrying 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 hydroaminationmethylation of 1-octene with diethanolamine as model substrates. Although water is both the condensation side product and the solvent, a proof of concept for catalyst recycling by simple decantation was shown.

The tandem-catalysed hydroaminationmethylation is a useful tool to synthesise linear amines from olefins and amines in an atom efficient manner. To enable the coupling of highly functionalised, hydroxyl-carrying 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 hydroaminationmethylation of 1-octene with diethanolamine as model substrates. Although water is both the condensation side product and the solvent, a proof of concept for catalyst recycling by simple decantation was shown.

The tandem-catalysed hydroaminationmethylation is a useful tool to synthesise linear amines from olefins and amines in an atom efficient manner. To enable the coupling of highly functionalised, hydroxyl-carrying 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 hydroaminationmethylation of 1-octene with diethanolamine as model substrates. Although water is both the condensation side product and the solvent, a proof of concept for catalyst recycling by simple decantation was shown.

The tandem-catalysed hydroaminationmethylation is a useful tool to synthesise linear amines from olefins and amines in an atom efficient manner. To enable the coupling of highly functionalised, hydroxyl-carrying 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 hydroaminationmethylation of 1-octene with diethanolamine as model substrates. Although water is both the condensation side product and the solvent, a proof of concept for catalyst recycling by simple decantation was shown.

The tandem-catalysed hydroaminationmethylation is a useful tool to synthesise linear amines from olefins and amines in an atom efficient manner. To enable the coupling of highly functionalised, hydroxyl-carrying 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 hydroaminationmethylation of 1-octene with diethanolamine as model substrates. Although water is both the condensation side product and the solvent, a proof of concept for catalyst recycling by simple decantation was shown.

The tandem-catalysed hydroaminationmethylation is a useful tool to synthesise linear amines from olefins and amines in an atom efficient manner. To enable the coupling of highly functionalised, hydroxyl-carrying 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 hydroaminationmethylation of 1-octene with diethanolamine as model substrates. Although water is both the condensation side product and the solvent, a proof of concept for catalyst recycling by simple decantation was shown.

The tandem-catalysed hydroaminationmethylation is a useful tool to synthesise linear amines from olefins and amines in an atom efficient manner. To enable the coupling of highly functionalised, hydroxyl-carrying 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 hydroaminationmethylation of 1-octene with diethanolamine as model substrates. Although water is both the condensation side product and the solvent, a proof of concept for catalyst recycling by simple decantation was shown.

The tandem-catalysed hydroaminationmethylation is a useful tool to synthesise linear amines from olefins and amines in an atom efficient manner. To enable the coupling of highly functionalised, hydroxyl-carrying 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 hydroaminationmethylation of 1-octene with diethanolamine as model substrates. Although water is both the condensation side product and the solvent, a proof of concept for catalyst recycling by simple decantation was shown.
Two novel reaction pathways were tested to synthesize the linear α,ω-C10-diester exclusively from three basic chemicals: 1,3-butanediol, carbon monoxide and methanol. Therefore, carboxylation of 1,3-butanediol and methanol were 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 carboxylatation, the C9-monester as intermediate could be formed in nearly quantitative yields and excellent linearity. In a second reaction step, the isolated monester was successfully converted by methoxy carbonylation into the desired linear C10-diester in overall yields up to 84%.
Still, the hydroamination of dienes to form allylic amines is a challenging task in a continuous operation. Herein, we present the proof of concept of a membrane reactor by the implementation of a continuously operated hydroamination reaction of β-mycene with morpholine. Via application of a poly ether -ether-ether-ketone (PEEK) membrane, operation at elevated temperatures was possible in an integrated reaction/separation unit. 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 achieved acting in a stable continuous operation. In the end an increase of the turnover number from 450 to 513 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-mycene above 93% was reached in a long-time stable process.

The bifunctional primary amine TCD-diamine (34)[(4R)-3(aminomethyl)-cyclodecane] is accessible by hydroformylation and amination with ammonia of commercially available decylpentane (cdpal) and offers many applications as a monomer building block. In this work a new simple and selective phosphorus-free and rhodium catalyzed bis-hydroaminomethylation (bis-HAM) of non-conjugated diolefins to secondary TCD-diamines for potential new adhesive or coating applications is reported. Key to a successful one phase bis-HAM is an access of amine and syngas pressure. For the cyclic diene dpal high conversion combined with very good yields of 94% TCD-dipalamin were achieved under optimised conditions. Transferability to other dienes and primary and secondary amines is effectively shown. This contribution presents the first time the successful development of an effective application of reactive extraction as a recycling and purification method, to recycle the performance of a rhodium metal catalyst and separate the diaminos. The ex-situ reactive-extraction of the bis-HAM product is conducted using aqueous acidic to form water soluble ammonium salt. The resulting ammonium salt is most present in the aqueous phase while the rhodium complex mainstains in the nonpolar organic phase and is successfully reused in three recycling runs.

Still, the hydroamination of dienes to form allylic amines is a challenging task in a continuous operation. Herein, we present the proof of concept of a membrane reactor by the implementation of a continuously operated hydroamination reaction of β-mycene with morpholine. Via application of a poly ether -ether-ether-ketone (PEEK) membrane, operation at elevated temperatures was possible in an integrated reaction/separation unit. 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 achieved acting in a stable continuous operation. In the end an increase of the turnover number from 450 to 513 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-mycene above 93% was reached in a long-time stable process.

The bifunctional primary amine TCD-diamine [34](4R)-3(aminomethyl)-cyclodecane] is accessible by hydroformylation and amination with ammonia of commercially available decylpentane (cdpal) and offers many applications as a monomer building block. In this work a new simple and selective phosphorus-free and rhodium catalyzed bis-hydroaminomethylation (bis-HAM) of non-conjugated diolefins to secondary TCD-diamines for potential new adhesive or coating applications is reported. Key to a successful one phase bis-HAM is an access of amine and syngas pressure. For the cyclic diene dpal high conversion combined with very good yields of 94% TCD-dipalamine were achieved under optimised conditions. Transferability to other dienes and primary and secondary amines is effectively shown. This contribution presents the first time the successful development of an effective application of reactive extraction as a recycling and purification method, to recycle the performance of a rhodium metal catalyst and separate the diaminos. The ex-situ reactive-extraction of the bis-HAM product is conducted using aqueous acidic to form water soluble ammonium salt. The resulting ammonium salt is most present in the aqueous phase while the rhodium complex mainstains in the nonpolar organic phase and is successfully reused in three recycling runs.

Still, the hydroamination of dienes to form allylic amines is a challenging task in a continuous operation. Herein, we present the proof of concept of a membrane reactor by the implementation of a continuously operated hydroamination reaction of β-mycene with morpholine. Via application of a poly ether -ether-ether-ketone (PEEK) membrane, operation at elevated temperatures was possible in an integrated reaction/separation unit. 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 achieved acting in a stable continuous operation. In the end an increase of the turnover number from 450 to 513 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-mycene above 93% was reached in a long-time stable process.
The lean biphasic aqueous hydroformylation without chemical additives of the long chain olefin 1-octene using the simple ligand triphenyl trifluoromethyl 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 higher turnover frequencies of 7,640 h⁻¹ the stirred tank reactor showed high space time yields of up to 12.6 kmolm⁻³ s⁻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 selectivity 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 1,b≥53 but with reduced catalytic activity.

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 telemerization of $\beta$-myrcene with N-methylglucamine to CuN$_2$-alkylated polyols, which show surface activity. The use of aqueous solvent systems along with amphiphilic ligands bridges the polarity gap and shows high reactivities.


Highlighted as cover picture
DOI: 10.1039/C7CY00398

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 telemerization of $\beta$-myrcene with N-methylglucamine to CuN$_2$-alkylated polyols, which show surface activity. The use of aqueous solvent systems along with amphiphilic ligands bridges the polarity gap and shows high reactivities.


Highlighted as cover picture DOI: 10.1002/cssc.201700977

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 ($\text{Rhl(dppe)}$) 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 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.


Temperaturegeführte Mehrkomponentenlösungsmittelgemische (TMLs) sind eine elegante Möglichkeit, homogene Katalysatoren vom Produkt abzutrennen und so zu rekyclieren. Im vorliegenden Beitrag wird die Entwicklung der TML vom Labor- bis in den kontinuierlichen Miniplant-Maßstab beschrieben und anhand von Beispielen genauer beleuchtet.


The application of homogeneous transition metal catalysis 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.
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.), hydrodearomatizations, 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.

This tandem catalysis system allows the hydroformylation/hydrogenation of intermediate aldehydes to selectively provide diols under mild reaction conditions. As model substrate, the industrial relevant dicyclopentadiene (dcpd) was chosen. With the reaction system [Rh(cyclooctene)2] and triethylamine diols are produced in 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 31.1 reaction. Finally, the Rh/amine catalyst complex was recycled by a simple water extraction of the diol product.

By applying a rhodium/BiPhePhos catalyst a high turnover frequency of 375 h⁻¹ and a high degree of isomer selectivity is achieved. This tandem catalysis 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 [Rh(cyclooctene)2] and triethylamine diols are produced in 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 31.1 reaction. Finally, the Rh/amine catalyst complex was recycled by a simple water extraction of the diol product.


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 tandem catalysis 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 [Rh(cyclooctene)2] and triethylamine diols are produced in 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 31.1 reaction. Finally, the Rh/amine catalyst complex was recycled by a simple water extraction of the diol product.

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 (2.1% of the initial amount) is very low. The catalyst was successfully recycled five times.


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 (2.1% of the initial amount) is very low. The catalyst was successfully recycled five times.
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 takes place at the surface. This study also underlines the importance of procedural optimization in multiphase reactions.

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 takes place at the surface. This study also underlines the importance of procedural optimization in multiphase reactions.
Resource efficient bio-hydroamomethylation of the castor oil derived renewables methylundecene 1-olefins 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 homogenous Rh-catalyst was recycled. Finally, polycrystallization yielded a novel piperazine-linked polyester.

The stable hydroformylation process with a yield of the linear product 55% is shown. While the Rh/Biphephos catalyst is recycled. Finally, polycondensation yielded 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 homogenous Rh-catalyst was recycled. Finally, polycrystallization yielded a novel piperazine-linked polyester.

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 long run. Low energy demand, high scalability as well as transferability to other reactions make this method promising for new industrial applications.
In order to design an innovative continuous process for the conversion of the renewable β-terpene myrcene, three methodical steps are shown in this paper to find a setup for the demanding homogeneously catalyzed hydrometallation. First step is the theoretical and practical design of a suitable thermomorphic multicomponent solvent (TMS) system for the recycling of 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 terpene terpenol ethers is achieved in 3 complete cycles. The results show that the TC reactor is suitable for the hydrometallation and generates high conversion and yields (X=82%, Y=80%). Recycling experiments were conducted successfully in the miniplant setup to show the long-term operation in a period of 24h.

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.

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 Ph/phosphine type catalysts were studied in depth, highly active Ph/NC catalysts have been studied in the telomerization almost exclusively along with methanol. In the course of employing alcohols form 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. Aliphatic 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 terpenoids to gain new allylic terpenol ethers.

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 constructual 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.

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.


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.


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/Bijpephos 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/d 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-dialkylpiperazines.


Abstract: Good things come in threes: A new auto-tandem catalytic process enables direct access to C6,α,ω-diesters from 2,7-octadienol by merging three different reaction sequences: ether formation, ether carboxylation and alkoxycarbonylation. Good yields of the desired diester are obtained with a Pd/Xantphos catalyst, which allows the direct use of allylic alcohols, thereby minimising waste production with water as the sole co-product.


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 alkoxycarbonylation 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.

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.


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.


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.


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 multiphase 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.

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-Biphosphes 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 a priori basis for TMS development.


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/L2-bis(2-tetrahydrofuran)bis(2,2,2-trifluoroethoxycarbonyl)acetic acid catalyst. Product yields up to 79% and a high regioselectivity of 98% 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.

2015


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 corresponding amides.


Abstract: The palladium-catalyzed aminocarbonylation of aliphatic amines is presented for the first time without the need for external CO pressure. N,N-dimethylformamide (DMF) is used as an in situ source of 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 isomerising carbonylations. The reaction pathway was investigated and proved to proceed by a CO catalyzed DMF decomposition to CO and dimethyl amine with subsequent amine-carbonylation of the alkene. Pressures of versus-time curves gave more insight into the correlation between acid concentration and amine carboxylation activity. Aliphatic amines (terminal and internal) are transformed, also in commercial scale, into the corresponding linear N,N-dimethylamides with excellent selectivities. Hence, amide synthesis by aminocarbonylation moves closer to application in standard organic laboratories.

Abstract: This paper describes the development of an efficient catalyst recycling approach for the iridium-catalyzed hydrosilylation of 1-octene through the investigation of biphasic systems, thermoregional solvent systems and an ex situ extraction. Particularly high selectivities (>90%) towards the desired aldehydes as well as low rates of iridium leaching were observed using the monosulfonated triphenylphosphine ligand (TTPP) in polar solvents such as pure water or N,N-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 N,N-dimethylformamide and the extraction with non-polar solvents.


Highlighted as cover picture DOI: 10.1002/ccct.201500912

Abstract: A highly selective catalyst system was developed for the recently discovered tandem hydroformylation/acyloin reaction to systematically 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 provided with comparable excellent selectivities up to >99% for the first and second reaction step, therefore a general synthesis pathway. 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.


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 developments. Four reactions, namely defunctionalisation, hydroformylation, defunctanisation and isomerisation, have been identified for transforming renewables in tandem reactions. Every reaction yields a reactive intermediate or a tailored selectivity in order to use the natural molecular structure of renewables.

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.


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.


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 in one pot. These diesters were successfully separated from the catalyst using thermomorphic solvent techniques, 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.

2013


**2012**


**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.


**Abstract:** Telomerization of common petrochemical 1,3-diienes 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.


**Abstract:** Easy accessible 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.


**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, hydromonomethylation, 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.

Prior 2011


**Abstract:** Mit nachwachsenden Rohstoffen lassen sich neue Produkte synthetisieren oder bei bekannten Produkten fossile Rohstoffe ersetzen. Die Katalyse macht viele Produktionswege erst möglich.


**Abstract:** Telomerization of common petrochemical 1,3-diienes 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.