Dynamic Cross-Exchange in Halophosphonium Species: Direct Observation of Stereochemical Inversion in the Course of an S_N2 Process

Dr. Kirill Nikitin, Dr. Elizabeth V. Jennings, Dr. Sulaiman Al Sulaimi, Dr. Yannick Ortin and Prof. Dr. Declan G. Gilheany

*Angew. Chem. Int. Ed. 2018, 57(6), 1480*

**Abstract**

The complex fluxional interconversions between otherwise very similar phosphonium bromides and chlorides R_3PX+X− (R=Alk, Ar, X=Cl or Br) were studied by NMR techniques. Their energy barriers are typically ca. 11 kcal mol⁻¹, but rise rapidly as bulky groups are attached to phosphorus, revealing the importance of steric factors. In contrast, electronic effects, as measured by Hammett analysis, are modest (ρ 1.46) but still clearly indicate negative charge flow towards phosphorus in the transition state. Most significantly, detailed analysis of the exchange pathways unequivocally, and for the first time in any such process, shows that nucleophilic attack of the nucleophilic anion on the tetrahedral centre results in inversion of configuration.

Pd-Catalyzed Enantioselective [6+4] Cycloaddition of Vinyl Oxetanes with Azadienes to Access Ten-Membered Heterocycles

Ya-Nong Wang, Li-Cheng Yang, Dr. Zi-Qiang Rong, Dr. Tang-Lin Liu, Ruoyang Liu and Prof. Yu Zhao

*Angew. Chem. Int. Ed. 2018, 57(6), 1596*

**Abstract**

We report herein the first enantioselective cycloaddition of vinyl oxetanes, the reaction of which with azadienes provided unprecedented access to ten-membered heterocycles through a [6+4] cycloaddition. By using a commercially available chiral Pd-SIPHOX catalyst, a wide range of benzofuran- as well as indole-fused heterocycles could be accessed in excellent yield and enantioselectivity. A unique Lewis acid induced fragmentation of these ten-membered heterocycles was also discovered.
**Palladium-Catalyzed Intramolecular Trost–Oppolzer-Type Alder–Ene Reaction of Dienyl Acetates to Cyclopentadienes**

Siddheshwar K. Bankar, Bara Singh, Pinku Tung and Prof. Dr. S. S. V. Ramasastry

*Angew. Chem. Int. Ed.* 2018, 57(6), 1678

Abstract

A new approach to the synthesis of highly substituted cyclopentadienes, indenes, and cyclopentene-fused heteroarenes by means of the Pd-catalyzed Trost–Oppolzer-type intramolecular Alder–ene reaction of 2,4-pentadienyl acetates is described. This unprecedented transformation combines the electrophilic features of the Tsuji–Trost reaction with the nucleophilic features of the Alder–ene reaction. The overall outcome can be perceived as a hitherto unknown “acid-free” iso-Nazarov-type cyclization. The versatility of this strategy was further demonstrated by the formal synthesis of paucifloral F, a resveratrol-based natural product.

**Synthesis of Phenols: Organophotoredox/Nickel Dual Catalytic Hydroxylation of Aryl Halides with Water**

Liu Yang, Prof. Dr. Zhiyan Huang, Dr. Gang Li, Prof. Dr. Wei Zhang, Prof. Dr. Rui Cao, Prof. Dr. Chao Wang, Prof. Dr. Jianliang Xiao and Prof. Dr. Dong Xue


Abstract

A highly effective hydroxylation reaction of aryl halides with water under synergistic organophotoredox and nickel catalysis is reported. The OH group of the resulting phenols originates from water, following deprotonation facilitated by an intramolecular base group on the ligand. Significantly, aryl bromides as well as less reactive aryl chlorides served as effective substrates to afford phenols with a wide range of functional groups. Without the need for a strong inorganic base or an expensive noble-metal catalyst, this process can be applied to the efficient preparation of diverse phenols and enables the hydroxylation of multifunctional pharmaceutically relevant aryl halides.
Barbier–Negishi Coupling of Secondary Alkyl Bromides with Aryl and Alkenyl Triflates and Nonaflates

Ke-Feng Zhang, Fadri Christoffel and Prof. Dr. Olivier Baudoin


**Abstract**

A mild and practical Barbier–Negishi coupling of secondary alkyl bromides with aryl and alkenyl triflates and nonaflates has been developed. This challenging reaction was enabled by the use of a very bulky imidazole-based phosphine ligand, which resulted in good yields as well as good chemoselectivity and site selectivities for a broad range of substrates at room temperature and under non-aqueous conditions. This reaction was extended to primary alkyl bromides by using an analogous pyrazole-based ligand.

Enantioselective Polyene Cyclization Catalyzed by a Chiral Bronsted Acid

Liwen Fan, Chunyu Han, Xuerong Li, Jiasheng Yao, Zhengning Wang, Chaochao Yao, Weihao Chen, Prof. Dr. Tao Wang and Prof. Dr. Junfeng Zhao

*Angew. Chem. Int. Ed.* **2018**, **57**(8), 2115

**Abstract**

The first enantioselective polyene cyclization initiated by a BINOL-derived chiral N-phosphoramidoamine (NPA) catalyzed protonation of an imine is described. The ion-pair formed between the iminium ion and chiral counter anion of the NPA plays an important role for controlling the stereochemistry of the overall transformation. This strategy offers a highly efficient approach to fused tricyclic frameworks containing three contiguous stereocenters, which are widely found in natural products. In addition, the first catalytic asymmetric total synthesis of (~)-ferruginol was accomplished with an NPA catalyzed enantioselective polyene cyclization, as the key step for the construction of the tricyclic core, with excellent yield and enantioselectivity.
**N-Substituted Hydrazones by Manganese-Catalyzed Coupling of Alcohols with Hydrazine: Borrowing Hydrogen and Acceptorless Dehydrogenation in One System**

Dr. Uttam Kumar Das, Yehoshoa Ben-David, Dr. Yael Diskin-Posner and Prof. David Milstein

*Angew. Chem. Int. Ed. 2018, 57(8), 2179*

**Abstract**

An unprecedented one-step synthesis of N-substituted hydrazones by coupling of alcohols with hydrazine is reported. This partial hydrogen-borrowing reaction is catalyzed by a new manganese pincer complex under mild reaction conditions, thus liberating water and dihydrogen as the only byproducts. Mechanistic insight, based on the observation of intermediates, is provided.

**Discovery and Enumeration of Organic-Chemical and Biomimetic Reaction Cycles within the Network of Chemistry**

Michał D. Bajczyk, Dr. Piotr Dittwald, Agnieszka Wołos, Sara Szymkuć and Prof. Bartosz A. Grzybowski

*Angew. Chem. Int. Ed. 2018, 57(9), 2367*

**Abstract**

Analysis of the chemical-organic knowledge represented as a giant network reveals that it contains millions of reaction sequences closing into cycles. Without realizing it, independent chemists working at different times have jointly created examples of cyclic sequences that allow for the recovery of useful reagents and for the autoamplification of synthetically important molecules, those that mimic biological cycles, and those that can be operated one-pot.
**Palladium-Catalyzed Asymmetric Aminohydroxylation of 1,3-Dienes**

Hong-Cheng Shen, Yu-Feng Wu, Ying Zhang, Lian-Feng Fan, Prof. Dr. Zhi-Yong Han and Prof. Dr. Liu-Zhu Gong

*Angew. Chem. Int. Ed.* 2018, 57(9), 2372

**Abstract**

A Pd$^{II}$-catalyzed asymmetric aminohydroxylation of 1,3-dienes with N-tosyl-2-aminophenols was developed by making use of a chiral pyridinebis(oxazoline) ligand. The highly regioselective reaction provides direct and efficient access to chiral 3,4-dihydro-2$^H$-1,4-benzoxazines in high yield and enantioselectivity (up to 96:4 e.r.). The reaction employs readily available N-tosyl-2-aminophenols as a unique aminohydroxylation reagent and is complementary to known asymmetric aminohydroxylation methods.

**Enzymatic Electrosynthesis of Alkanes by Bioelectrocatalytic Decarbonylation of Fatty Aldehydes**

Dr. Sofiene Abdellaoui, Dr. Florika C. Macazo, Rong Cai, Dr. Antonio L. De Lacey, Dr. Marcos Pita and Prof. Shelley D. Minteer

*Angew. Chem. Int. Ed.* 2018, 57(9), 2404

**Abstract**

An enzymatic electrosynthesis system was created by combining an aldehyde deformylating oxygenase (ADO) from cyanobacteria that catalyzes the decarbonylation of fatty aldehydes to alkanes and formic acid with an electrochemical interface. This system is able to produce a range of alkanes (octane to propane) from aldehydes and alcohols. The combination of this bioelectrochemical system with a hydrogenase bioanode yields a $\mathrm{H}_2$/heptanal enzymatic fuel cell (EFC) able to simultaneously generate electrical energy with a maximum current density of 25 $\mu\text{A cm}^{-2}$ at 0.6 V and produce hexane with a faradaic efficiency of 24 %.
**Reductive Amination by Photoredox Catalysis and Polarity-Matched Hydrogen Atom Transfer**

Dr. Xingwei Guo and Prof. Dr. Oliver S. Wenger


**Abstract**

The excitation of a Ru\(^{II}\) photosensitizer in the presence of ascorbic acid leads to the reduction of iminium ions to electron-rich \(\alpha\)-aminoalkyl radical intermediates, which are rapidly converted into reductive amination products by thiol-mediated hydrogen atom transfer (HAT). As a result, the reductive amination of carbonyl compounds with amines by photoredox catalysis proceeds in good to excellent yields and with broad substrate scope and good functional group tolerance. The three key features of this work are 1) the rapid interception of electron-rich \(\alpha\)-aminoalkyl radical intermediates by polarity-matched HAT in a photoredox reaction, 2) the method of reductive amination by photoredox catalysis itself, and 3) the application of this new method for temporally and spatially controlled reactions on a solid support, as demonstrated by the attachment of a fluorescent dye on an activated cellulose support by photoredox-catalyzed reductive amination.
Insights into the Catalytic Activity of [Pd(NHC)(cin)Cl] (NHC=IPr, IPrCl, IPrBr) Complexes in the Suzuki–Miyaura Reaction

Dr. Frédéric Izquierdo, Caroline Zinser, Dr. Yury Minenkov, Dr. David B. Cordes, Prof. Alexandra M. Z. Slawin, Prof. Luigi Cavallo, Dr. Fady Nahra, Dr. Catherine S. J. Cazin and Prof. Dr. Steven P. Nolan

ChemCatChem 2018, 10(3), 601

Abstract

The influence of C4,5-halogenation on palladium N-heterocyclic carbene complexes and their activity in the Suzuki–Miyaura reaction were investigated. Two [Pd(NHC)(cin)Cl] complexes bearing IPrCl and IPrBr ligands (IPr=1,3-bis(2,6-diisopropyl-phenyl)imidazol-2-ylidene; cin=cinnamyl) were synthesized. After determining the electronic and steric properties of these ligands, their properties were compared to those of [Pd(IPr)(cin)Cl]. The three palladium complexes were studied by using DFT calculations to delineate their behavior in the activation step leading to the putative 12-electron active catalyst. Experimentally, their catalytic activity in the Suzuki–Miyaura reaction involving a wide range of coupling partners (30 entries) at low catalyst loading was studied.


Dr. Viktor Mojr, Gabriela Pitrová, Karolína Straková, Dr. Dorota Prukala, Sabina Brazevic, Dr. Eva Svobodová, Dr. Irena Hoskovcová, Dr. Gotard Burdziński, Dr. Tomáš Slanina, Prof. Dr. Marek Sikorski and Prof. Dr. Radek Cibulka

ChemCatChem 2018, 10(3), 849

Abstract

New photocatalysts from the flavin family were found to mediate the [2+2] photocycloaddition reaction. 3-Butyl-10-methyl-5-deazaflavin (3a) and 1-butyl-7,8-dimethoxy-3-methylalloxazine (2e), if irradiated by visible light, were shown to allow an efficient (Φ≈3–10 %) intramolecular cyclisation of various types of substrates including substituted styrene dienes and bis(aryl enones), considered as electron-rich and electron-poor substrates, respectively, without any additional reagent. The versatility of the procedure was demonstrated by the cyclisation of photosensitive cinnamyl (E)-3-iodoallyl ether. Structure–activity studies found alloxazine 2e was more active than 7-monosubstituted (R=Cl, Br and MeO) alloxazines. The introduction of chlorine and bromine atom on the deazaflavin skeleton did not enhance the catalytic efficiency of 3a. A detailed electrochemical and spectroscopic study explains the reaction mechanism proceeding through energy transfer from the flavin excited triplet state to the diene followed by its cyclisation.

David W. Flaherty

*ACS Catal.*, 2018, 8 (2), pp 1520–1527

Selective Hydrogenation of Carboxylic Acids to Alcohols or Alkanes Employing a Heterogeneous Catalyst

J. Ullrich, B. Breit

*ACS Catal.*, 2018, 8 (2), pp 785–789

The chemoselective hydrogenation of carboxylic acids to either alcohols or alkanes is reported, employing a heterogeneous bimetallic catalyst consisting of rhenium and palladium supported on graphite. α-Chiral carboxylic acids were hydrogenated without loss of optical purity. The catalyst displays a reverse order of reactivity upon hydrogenation of different carboxylic functions with esters being less reactive than amides and carboxylic acids. This allows for chemoselective hydrogenation of an acid in the presence of an ester or an amide function.

An Active Alkali-Exchanged Faujasite Catalyst for p-Xylene Production via the One-Pot Diels–Alder Cycloaddition/Dehydration Reaction of 2,5-Dimethylfuran with Ethylene


*ACS Catal.*, 2018, 8 (2), pp 760–769

The one-pot Diels–Alder cycloaddition (DAC)/dehydration (D) tandem reaction between 2,5-dimethylfuran and ethylene is a potent pathway toward biomass-derived p-xylene. In this work, we present a cheap and active low-silica potassium-exchanged faujasite (KY, Si/Al = 2.6) catalyst. Catalyst optimization was guided by a computational study of the DAC/D reaction mechanism over different alkali-exchanged faujasites using periodic density functional theory calculations complemented by microkinetic modeling. Two types of faujasite models were compared, i.e., a high-silica alkali-exchanged faujasite model representing isolated active cation sites and a low-silica alkali-exchanged faujasite in which the reaction involves several cations in the proximity. The mechanistic study points to a significant synergetic cooperative effect of the ensemble of cations in the faujasite supercage on the DAC/D reaction. Alignment of the reactants by their interactions with the cationic
sites and stabilization of reaction intermediates contribute to the high catalytic performance. Experiments confirmed the prediction that KY is the most active catalyst among low-silica alkali-exchanged faujasites. This work is an example of how the catalytic reactivity of zeolites depends on multiple interactions between the zeolite and reagents.

**Quaternary Alkyl Ammonium Salt-Catalyzed Transformation of Glycidol to Glycidyl Esters by Transesterification of Methyl Esters**


*ACS Catal.*, 2018, 8 (2), pp 1097–1103

Catalytic transformation of glycidol while maintaining its epoxide moiety intact is challenging because the terminal epoxide that interacts with the hydroxyl group via a hydrogen bond is labile for the ring-opening reaction. We found that a quaternary alkyl ammonium salt catalyzes the selective transformation of glycidol to glycidyl esters by transesterification of methyl esters. The developed method can be applied to the synthesis of multiglycidyl esters, which are valuable epoxy resin monomers. Mechanistic studies revealed the formation of a binding complex of glycidol and quaternary alkyl ammonium salt in a nonpolar solvent and the generation of the alkoxide anion as a catalyst through the ring-opening reaction of the epoxide. Computational studies of the reaction mechanism indicated that the alkoxide anion derived from glycidol tends to abstract the proton of another glycidol rather than work as a nucleophile, initiating the catalytic transesterification. Payne rearrangement of the deprotonated glycidol, which produces a destabilized base that promotes nonselective reactions, is energetically unfavorable due to the double hydrogen bond between the anion and diol. The minimal interaction between the quaternary alkyl ammonium cation and the epoxide moiety inhibited the random ring-opening pathway leading to polymerization.

**Carbon Modification of Nickel Catalyst for Depolymerization of Oxidized Lignin to Aromatics**

M. Wang, X. Zhang, H. Li, J. Lu, M. Liu, F. Wang

*ACS Catal.*, 2018, 8 (2), pp 1614–1620

Catalytic valorization of lignin is a sustainable way to provide aromatics for the human society, which depends on the electronic structure of catalytic sites. We herein report the preparation of a carbon-modified nickel catalyst via carbothermal reduction of Ni-doped layered double hydroxides. Lignosulfonate (LS), a lignin resource from the pulp industry, was used as a renewable carbon precursor. The carbon residues in the nickel surface layer changed the 3d electron distribution of nickel, which was highly selective for the C–O bond hydrogenolysis of lignin into aromatics, and 22 wt % total mass yields of aromatics were achieved from hydrogenolysis of oxidized birch lignin.
Pd-Catalyzed, ortho C–H Methylation and Fluorination of Benzaldehydes Using Orthanilic Acids as Transient Directing Groups

X.-Y. Chen, E. J. Sorensen


The direct, Pd-catalyzed ortho C–H methylation and fluorination of benzaldehydes have been accomplished using commercially available orthanilic acids as transient directing groups. In these reactions, the 1-fluoro-2,4,6-trimethylpyridinium salts can be either a bystanding F⁺ oxidant or an electrophilic fluorinating reagent. An X-ray crystal structure of a benzaldehyde ortho C–H palladation intermediate was obtained using triphenylphosphine as the stabilizing ligand.

Half-Sandwich Ruthenium Carbene Complexes Link trans-Hydrogenation and gem-Hydrogenation of Internal Alkynes


The hydrogenation of internal alkynes with [Cp*Ru]-based catalysts is distinguished by an unorthodox stereochemical course in that E-alkenes are formed by trans-delivery of the two H atoms of H₂. A combined experimental and computational study now provides a comprehensive mechanistic picture: a metallacyclopropene (η2-vinyl complex) is primarily formed, which either evolves into the E-alkene via a concerted process or reacts to give a half-sandwich ruthenium carbene; in this case, one of the C atoms of the starting alkyne is converted into a methylene group. This transformation represents a formal gem-hydrogenation of a π-bond, which has hardly any precedent. The barriers for trans-hydrogenation and gem-hydrogenation are similar: whereas DFT predicts a preference for trans-hydrogenation, CCSD(T) finds gem-hydrogenation slightly more facile. The carbene, once formed, will bind a second H₂ molecule and evolve to the desired E-alkene, a positional alkene isomer or the corresponding alkane; this associative pathway explains why double bond isomerization and over-reduction compete with trans-hydrogenation. The computed scenario concurs with para-hydrogen-induced polarization transfer (PHIP) NMR data, which confirm direct trans-delivery of H₂, the formation of carbene intermediates by gem-hydrogenation, and their evolution into product and side products alike. Propargylic –OR (R = H, Me) groups exert a strong directing and stabilizing effect, such that several carbene intermediates could be isolated and characterized by X-ray diffraction. The gathered information spurred significant preparative advances: specifically, highly selective trans-hydrogenations of propargylic alcohols are reported, which are compatible with many other reducible functional groups. Moreover, the ability to generate metal carbenes by gem-hydrogenation paved the way for noncanonical hydrogenative cyclopropanations, ring expansions, and cycloadditions.
Evaluating differences in the active-site electronics of supported Au nanoparticle catalysts using Hammett and DFT studies


*Nature Chemistry, 2018, 10, 268.*

Abstract
Supported metal catalysts, which are composed of metal nanoparticles dispersed on metal oxides or other high-surface-area materials, are ubiquitous in industrially catalysed reactions. Identifying and characterizing the catalytic active sites on these materials still remains a substantial challenge, even though it is required to guide rational design of practical heterogeneous catalysts. Metal–support interactions have an enormous impact on the chemistry of the catalytic active site and can determine the optimum support for a reaction; however, few direct probes of these interactions are available. Here we show how benzyl alcohol oxidation Hammett studies can be used to characterize differences in the catalytic activity of Au nanoparticles hosted on various metal-oxide supports. We combine reactivity analysis with density functional theory calculations to demonstrate that the slope of experimental Hammett plots is affected by electron donation from the underlying oxide support to the Au particles.
Pt/Cu single-atom alloys as coke-resistant catalysts for efficient C–H activation


Nature Chemistry, 2018, 10, 325.

Abstract
The recent availability of shale gas has led to a renewed interest in C–H bond activation as the first step towards the synthesis of fuels and fine chemicals. Heterogeneous catalysts based on Ni and Pt can perform this chemistry, but deactivate easily due to coke formation. Cu-based catalysts are not practical due to high C–H activation barriers, but their weaker binding to adsorbates offers resilience to coking. Using Pt/Cu single-atom alloys (SAAs), we examine C–H activation in a number of systems including methyl groups, methane and butane using a combination of simulations, surface science and catalysis studies. We find that Pt/Cu SAAs activate C–H bonds more efficiently than Cu, are stable for days under realistic operating conditions, and avoid the problem of coking typically encountered with Pt. Pt/Cu SAAs therefore offer a new approach to coke-resistant C–H activation chemistry, with the added economic benefit that the precious metal is diluted at the atomic limit.
Palladium-catalysed anti-Markovnikov selective oxidative amination

Daniel G. Kohler, Samuel N. Gockel, Jennifer L. Kennemur, Peter J. Waller & Kami L. Hull

*Nature Chemistry, 2018, 10, 333.*

**Abstract**

In recent years, the synthesis of amines and other nitrogen-containing motifs has been a major area of research in organic chemistry because they are widely represented in biologically active molecules. Current strategies rely on a multistep approach and require one reactant to be activated prior to the carbon–nitrogen bond formation. This leads to a reaction inefficiency and functional group intolerance. As such, a general approach to the synthesis of nitrogen-containing compounds from readily available and benign starting materials is highly desirable. Here we present a palladium-catalysed oxidative amination reaction in which the addition of the nitrogen occurs at the less-substituted carbon of a double bond, in what is known as *anti*-Markovnikov selectivity. Alkenes are shown to react with imides in the presence of a palladate catalyst to generate the terminal imide through *trans*-aminopalladation. Subsequently, olefin isomerization occurs to afford the thermodynamically favoured products. Both the scope of the transformation and mechanistic investigations are reported.
Asymmetric transfer hydrogenation by synthetic catalysts in cancer cells

James P. C. Coverdale, Isolda Romero-Canelón, Carlos Sanchez-Cano, Guy J. Clarkson, Abraha Habtemariam, Martin Wills & Peter J. Sadler

*Nature Chemistry, 2018, 10, 347.*

**Abstract**

Catalytic anticancer metallodrugs active at low doses could minimize side-effects, introduce novel mechanisms of action that combat resistance and widen the spectrum of anticancer-drug activity. Here we use highly stable chiral half-sandwich organometallic Os(II) arene sulfonyl diamine complexes, [Os(arene)(TsDPEN)] (TsDPEN, N-(p-toluenesulfonyl)-1,2-diphenylethylene diamine), to achieve a highly enantioselective reduction of pyruvate, a key intermediate in metabolic pathways. Reduction is shown both in aqueous model systems and in human cancer cells, with non-toxic concentrations of sodium formate used as a hydride source. The catalytic mechanism generates selectivity towards ovarian cancer cells versus non-cancerous fibroblasts (both ovarian and lung), which are commonly used as models of healthy proliferating cells. The formate precursor N-formylmethionine was explored as an alternative to formate in PC3 prostate cancer cells, which are known to overexpress a deformylase enzyme. Transfer-hydrogenation catalysts that generate reductive stress in cancer cells offer a new approach to cancer therapy.
Inedible saccharides: a platform for CO2 capturing


Chemical Science 2017, 9, 1088.

Abstract

The economic viability of eco-friendly and renewable materials promotes the development of an alternative technology for climate change mitigation. Investigations reported over the past few years have allowed understanding the mechanism of action for a wide spectrum of saccharides toward carbon dioxide (CO₂), in terms of reactivity, reversibility, stability and uptake. Exploiting bio-renewables, viz., inedible saccharides, to reduce the anthropogenic carbon footprint upon providing a sustainable and promising technology that is of interest to different groups of scientists, to overcome demerits associated with the current state-of-the-art aqueous amine scrubbing agents, following a “green chemistry guideline”, by employing materials with properties relevant to the environment toward sustainable development. The interdisciplinary nature of research in this area provides a large body of literature that would meet the interest of the broad readership of different multidisciplinary fields. Although many reports emphasize the use of biomass in various industrial products ranging from pharmaceutics, medical preparations, soaps, textiles, cosmetics, household cleaners, and so on, to our knowledge there is no focused article that addresses the application of saccharides for CO₂ sequestration. In this review, we highlight the recent advances on the use of oligo-, poly- and cyclic saccharides to achieve a reversible binding of CO₂. The future research directions are discussed to provide insight toward achieving sustainable development through implementing bio-renewables.
Alkylative kinetic resolution of vicinal diols under phase-transfer conditions: a chiral ammonium borinate catalysis

M. Pawliczek, T. Hashimoto, K. Maruoka

Chemical Science 2018, 9, 1231.

Abstract

Herein, we report the first alkylative kinetic resolution of vicinal alcohols realized by cooperative use of a chiral quaternary ammonium salt and an achiral borinic acid. In addition, a catalytic regioselective alkylation of a secondary alcohol in the presence of an unprotected primary one is presented, emphasizing the unique selectivity and potential of this ammonium borinate catalysis.

Exploring the role of ionic liquids to tune the polymorphic outcome of organic compounds

Q. Zeng, A. Mukherjee, P. Müller, R. D. Rogers, A. S. Myerson

Chemical Science 2018, 9, 1510.

Abstract

While molecular solvents are commonly used in the screening of polymorphs, the choices are often restricted. Ionic liquids (ILs) — also referred as *designer solvents* — have immense possibility in this regard because of their wide flexibility of tunability. More importantly, the interactions among the IL components are completely unique compared to those present in the molecular solvents. In this context, we have chosen tetrolic acid (TA) and isonicotinamide (INA), which showed solution-structure link in molecular solvents in the past, as probes to investigate the role of imidazolium based ionic liquids in the polymorphism of these two systems and whether the different solute–solvent interactions in ILs affect the polymorphic outcome. It is observed that the selected imidazolium-based ILs, with varying anion basicity have influenced the crystallization outcome by the interaction between ILs and model compounds. Later, we have utilized the concept of double salt ionic liquids (DSIL) for INA, a penta-morphic system, to investigate the variation in the polymorphic outcome. This approach helped to obtain the forms that were otherwise inaccessible in ILs.
Photoinduced oxidative activation of electron-rich arenes: alkenylation with H₂ evolution under external oxidant-free conditions

X. Hu, G. Zhang, F. Bu, X. Luo, K. Yi, H. Zhang, A. Lei

Chemical Science 2018, 9, 1521.

Abstract

The dehydrogenative cross-coupling of arenes and alkenes is a particularly ideal approach for the synthesis of aryl alkenes. Herein, we report a photo-induced C–H/C–H cross-coupling between electron-rich arenes and styrene derivatives using a dual catalytic system containing an acridinium photosensitizer and a cobaloxime proton-reducing catalyst. This catalytic system enables the Csp²–Csp² bond formation accompanying H₂ evolution. Various substituted aryl alkenes can be afforded with good to excellent yields and high β-regioselectivity.

High throughput reaction screening using desorption electrospray ionization mass spectrometry


Chemical Science 2017, 9, 1647.

Abstract

We report the high throughput analysis of reaction mixture arrays using methods and data handling routines that were originally developed for biological tissue imaging. Desorption electrospray ionization (DESI) mass spectrometry (MS) is applied in a continuous on-line process at rates that approach 10⁴ reactions per h at area densities of up to 1 spot per mm² (6144 spots per standard microtiter plate) with the sprayer moving at ca. 10⁴ microns per s. Data are analyzed automatically by MS using in-house software to create ion images of selected reagents and products as intensity plots in standard array format. Amine alkylation reactions were used to optimize the system performance on PTFE membrane substrates using methanol as the DESI spray/analysis solvent. Reaction times can be <100 μs when reaction acceleration occurs in microdroplets, enabling the rapid screening of processes like N-alkylation and Suzuki coupling reactions as reported herein. Products and by-products were confirmed by on-line MS/MS upon rescanning of the array.
A strategy of ketalization for the catalytic selective dehydration of biomass-based polyols over H-beta zeolite

Penghua Che, Fang Lu, Xiaoqin Si, Hong Ma, Xin Nie and Jie Xu

Green Chem., 2018, 20, 634-640

Abstract

Biomass contains plentiful hydroxyl groups that lead to an oxygen-rich structure compared to petroleum-based chemicals. Dehydration is the most energy-efficient technique to remove oxygen; however, multiple similar vicinal hydroxyl groups in sugar alcohols impose significant challenges for their selective dehydration. Here, we present a novel strategy to control the etherification site in sugar alcohols by the ketalization of the vicinal-diol group for the highly selective formation of tetrahydrofuran derivatives. A ketone firstly reacts with terminal vicinal hydroxyl groups to form the 1,3-dioxolane structure. This structure of the constrained 1,3-dioxolane ring would improve the accessibility of reactive groups to facilitate intramolecular etherification. As a better leaving group than water, the ketone can also promote intramolecular etherification. Consequently, a range of tetrahydrofuran derivatives are produced in excellent yields with the H-beta zeolite catalyst under mild reaction conditions. This strategy opens up new opportunities for the efficient upgrading of biomass via the modification or protection of hydroxyl groups.
Transformation of cellulose and related carbohydrates into lactic acid with bifunctional Al(III)–Sn(II) catalysts

Weiping Deng, Pan Wang, Binju Wang, Yanliang Wang, Longfei Yan, Yanyun Li, Qinghong Zhang, Zexing Cao and Ye Wang

Green Chem., 2018, 20, 735-744

Abstract

The catalytic transformation of cellulose into valuable chemicals such as lactic acid under mild conditions represents a promising route for the efficient utilization of renewable biomass. Here, we report that the combination of Al(III) and Sn(II) cations can efficiently catalyse the conversion of cellulose and related carbohydrates into lactic acid in water. Al(III)–Sn(II) is the most efficient combination for lactic acid formation among the many dual cations investigated. Al(III) and Sn(II) with a molar ratio of 1/1 work cooperatively, providing lactic acid with yields of 90%, 81% and 65% in the conversions of fructose, glucose and cellulose, respectively. The formation of lactic acid involves a series of tandem steps including the hydrolysis of cellulose to glucose, the isomerisation of glucose to fructose, the retro-aldol fragmentation of fructose to C3 intermediates and the subsequent conversion of the C3 intermediates to lactic acid. Our experimental and computational studies suggest that Al(III) mainly catalyses the isomerisation of glucose or the C3 intermediates, whereas Sn(II) is primarily responsible for the retro-aldol fragmentation. The combination of the two cations enables the reaction to proceed smoothly with few side reactions, providing outstanding catalytic performances for lactic acid production from cellulose or the related carbohydrates.
Lignin extraction and catalytic upgrading from genetically modified poplar

Hao Luo and Mahdi M. Abu-Omar

Green Chem., 2018, 20, 745-753

Abstract

Lignin as the only natural resource of aromatics has the potential to be the feedstock of choice for the production of value-added chemicals. However, the recalcitrance of lignin has limited its valorization into value-added products, and it is often burned for heat. The acid-catalyzed organosolv extraction of lignin results in the formation of interunit carbon–carbon bonds, which limit its upgrading. In this work, three different solvent systems (methanol, acetone, and acetic acid) were evaluated for the extraction of native lignin from wild-type and genetically modified poplar species (wild type, high-S, and low-S). Over 68% of the original lignin in the biomass was isolated and subjected to further upgrading over a heterogeneous Ni/C catalyst (10 wt% of catalyst in methanol solvent, under 35 bar H2 pressure at 225 °C). Three major monomeric phenolic products, guaiacol, isoeugenol, and 4-propenyl syringol, were obtained. Methanol-extracted lignin gave the best yield of >60% of the said aromatic products. Methanol as a nucleophile reacted with the Cα benzylic carbocation formed during the organosolv extraction, minimizing the carbon–carbon bond formation. This protection by methanol was demonstrated by NMR spectroscopy. Scanning electron microscopy (SEM) images showed differences in the isolated lignin on the micron scale from the three different treatments.

Biomass pretreatment using deep eutectic solvents from lignin derived phenols

Kwang Ho Kim, Tanmoy Dutta, Jian Sun, Blake Simmons and Seema Singh
Abstract

In future biorefineries, the development of inexpensive and renewable reagents is highly desirable. In this work, we report a renewable and new class of deep eutectic solvent (DES) synthesized from lignin-derived phenolic compounds. Novel DESs tested in this work showed their potential as solvents for biomass pretreatment in terms of lignin removal and sugar release after enzymatic saccharification. The recycling and reusability of DESs were also evaluated. The results from this study prove that DESs synthesized from renewable resources are promising solvents for future biorefineries.
Abstract

Lignin, an aromatic biopolymer, is the main by-product of pulp manufacture, and has been under intense study, as it offers great promise as an alternative for petrochemical polymers. However due to its heterogeneity, the applications where lignin can be used have been limited, leading to the vast majority of it being burned for fuel. Colloidal lignin particles (CLPs) offer a means to disperse lignin homogenously into both water and other media, such as polymers. However, no means thus far have been presented that would allow for a large-scale production of CLPs. Herein we show an industrially scalable closed cycle process of CLP production. In the process, a concentrated solution of lignin in tetrahydrofuran (THF) and ethanol (EtOH) is added into the non-solvent water, instantaneously forming CLPs through self-assembly. The organic solvents are recovered and reused in the process. The aqueous CLPs are concentrated by ultrafiltration and the concentrated particles are spray dried, leading to redispersible microclusters. CLPs can be used in multiple applications, such as Pickering emulsions and composite materials. A significant portion of the 50 million tons of lignin produced by the pulp industry could be made into CLPs with this low cost process, which would open a whole new class of materials for industrial applications.
Direct catalytic conversion of glucose and cellulose

Zhenhuan Li, Kunmei Su, Jun Ren, Dongjiang Yang, Bowen Cheng, Chan Kyung Kim and Xiangdong Yao

Green Chem., 2018, 20, 863-872

Abstract

Biomass product 5-hydroxymethylfurfural (5-HMF) can be used to synthesize a broad range of value added compounds currently derived from petroleum. Thus, the effective conversion of glucose or cellulose (the major components of biomass) into fuels and chemical commodities has been capturing increasing attention. Previous studies have been extensively focused on a two-step process for producing 5-HMF from glucose or cellulose, i.e., the isomerization of glucose into fructose and then the dehydration of fructose. We herein discovered that heterogeneous sulfonated poly(phenylene sulfide) (SPPS) containing strong Brønsted acid sites is able to convert glucose and cellulose into 5-HMF with a high yield in ionic liquids (ILs). The optimal activity of glucose conversion to 5-HMF achieves a yield of 87.2% after 4 h reaction at 140 °C. For direct cellulose conversion, a 5-HMF yield of 68.2% can be achieved. The reaction mechanism over the SPPS catalyst in ILs was studied by DFT calculations, and the results indicated that the SO3H group of SPPS plays a crucial role in glucose conversion into 5-HMF, and it acts as a proton donor as a Brønsted acid and functions as a proton acceptor as the conjugate base. Furthermore, the anions and cations of ILs together with SO3H-SPPS helped in stabilizing the reaction intermediates and transition states, which also resulted in glucose facile conversion into 5-HMF. The new catalyst system highlights new opportunities offered by optimizing the production of 5-HMF directly from glucose and cellulose.
Acid-Catalyzed Conversion of Carbohydrates into Value-Added Small Molecules in Aqueous Media and Ionic Liquids

I. Bodachivskyi, U. Kuzhiumpambil, D. B. G. Williams


Biomass is the only realistic major alternative source (to crude oil) of hydrocarbon substrates for the commercial synthesis of bulk and fine chemicals. Within biomass, terrestrial sources are the most accessible, and therein lignocellulosic materials are most abundant. Although lignin shows promise for the delivery of certain types of organic molecules, cellulose is a biopolymer with significant potential for conversion into high-volume and high-value chemicals. This review covers the acid-catalyzed conversion of lower value (poly)carbohydrates into valorized organic building-block chemicals (platform molecules). It focuses on those conversions performed in aqueous media or ionic liquids to provide the reader with a perspective on what can be considered a best case scenario, that is, that the overall process is as sustainable as possible.
Polyethylene terephthalate that is 100% bioderived is in high demand in the market guided by the ever-more exigent sustainability regulations with the challenge of producing renewable terephthalic acid remaining. Renewable terephthalic acid or its precursors can be obtained by Diels–Alder cycloaddition and further dehydrogenation of biomass-derived muconic acid. The cis,cis isomer of the dicarboxylic acid is typically synthesized by fermentation with genetically modified microorganisms, a process that requires complex separations to obtain a high yield of the pure product. Furthermore, the cis isomer has to be transformed into the trans,trans form and has to be esterified before it is suitable for terephthalate synthesis. To overcome these challenges, we investigated the synthesis of dialkyl muconates by cross-metathesis. The Ru-catalyzed cross-coupling of sorbates with acrylates, which can be bioderived, proceeded selectively to yield diester muconates in up to 41% yield by using very low catalyst amounts (0.5–3.0 mol %) and no solvent. In the optimized procedure, the muconate precipitated as a solid and was easily recovered from the reaction medium. Analysis by GC–MS and NMR spectroscopy showed that this method delivered exclusively the trans,trans isomer of dimethyl muconate. The Diels–Alder reaction of dimethyl muconate with ethylene was studied in various solvents to obtain 1,4-bis(carbomethoxy)cyclohexene. The cycloaddition proceeded with very high conversions (77–100%) and yields (70–98%) in all of the solvents investigated, and methanol and tetrahydrofuran were the best choices. Next, the aromatization of 1,4-bis(carbomethoxy)cyclohexene to dimethyl terephthalate over a Pd/C catalyst resulted in up to 70% yield in tetrahydrofuran under an air atmosphere. Owing to the high yield of the reaction of dimethyl muconate to 1,4-bis(carbomethoxy)cyclohexene, no separation step was needed before the aromatization. This is the first time that cross-metathesis is used to produce bioderived trans,trans-muconates as precursors to renewable terephthalates, important building blocks in the polymer industry.
Solubilization and Upgrading of High Polyethylene Terephthalate Loadings in a Low-Costing Bifunctional Ionic Liquid

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The solubilization and efficient upgrading of high loadings of polyethylene terephthalate (PET) are important challenges, and most solvents for PET are highly toxic. Herein, a low-cost (ca. $1.2 \text{ kg}^{-1}$) and biocompatible ionic liquid (IL), cholinium phosphate ([Ch]3[PO4]), is demonstrated for the first time to play bifunctional roles in the solubilization and glycolytic degradation of PET. A high loading of PET (10 wt %) was readily dissolved in [Ch]3[PO4] at relatively low temperatures (120 °C, 3 h) and under water-rich conditions. In-depth analysis of the solution revealed that high PET solubilization in [Ch]3[PO4] could be ascribed to significant PET depolymerization. Acid precipitation yielded terephthalic acid as the dominant depolymerized monomer with a theoretical yield of approximately 95 %. Further exploration showed that in the presence of ethylene glycol (EG), the [Ch]3[PO4]-catalyzed glycolysis of PET could efficiently occur with approximately 100 % conversion of PET and approximately 60.6 % yield of bis(2-hydroxyethyl)terephthalate under metal-free conditions. The IL could be reused at least three times without an apparent decrease in activity. NMR spectroscopy analysis revealed that strong hydrogen-bonding interactions between EG and the IL played an important role in the activation of EG and promotion of the glycolysis reaction. This study opens up avenues for exploring environmentally benign and efficient IL technology for solubilizing and recycling postconsumer polyester plastics.
Towards Sustainable H2 Production: Rational Design of Hydrophobic Triphenylamine-based Dyes for Sensitized Ethanol Photoreforming


Donor–acceptor dyes are a well-established class of photosensitizers, used to enhance visible-light harvesting in solar cells and in direct photocatalytic reactions, such as H2 production by photoreforming of sacrificial electron donors (SEDs). Amines—typically triethanolamine (TEOA)—are commonly employed as SEDs in such reactions. Dye-sensitized photoreforming of more sustainable, biomass-derived alcohols, on the other hand, was only recently reported by using methanol as the electron donor. In this work, several rationally designed donor–acceptor dyes were used as sensitizers in H2 photocatalytic production, comparing the efficiency of TEOA and EtOH as SEDs. In particular, the effect of hydrophobic chains in the spacer and/or the donor unit of the dyes was systematically studied. The H2 production rates were higher when TEOA was used as SED, whereas the activity trends depended on the SED used. The best performance was obtained with TEOA by using a sensitizer with just one bulky hydrophobic moiety, propylenedioxythiophene, placed on the spacer unit. In the case of EtOH, the best-performing sensitizers were the ones featuring a thiazolo[5,4-d]thiazole internal unit, needed for enhancing light harvesting, and carrying alkyl chains on both the donor part and the spacer unit. The results are discussed in terms of reaction mechanism, interaction with the SED, and structural/electrochemical properties of the sensitizers.
An Efficient Metal-Free Catalyst for Oxidative Dehydrogenation Reaction: Activated Carbon Decorated with Few-Layer Graphene

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ChemSusChem 2018, 11, 536

Activated carbon (AC) has been widely used in the catalysis field because of its low cost, scalable production, high specific surface area, and abundant exposed edge. Because of the amorphous structure, traditional AC is unstable in presence of O2 at high temperature, which hinders the application of AC catalysts in oxidative dehydrogenation (ODH) of alkanes. Here, partially graphitic AC decorated with few-layer graphene is facilely fabricated by simple high-temperature calcination. The graphitic transformation significantly enhances the antioxidation property, long-term stability of AC during the ODH reaction, and especially dramatically increases the graphitic edge areas in which the active ketonic carbonyl groups are selectively formed in ODH reactions. A high reactivity with 41.5 % selectivity and 13.2 % yield to C4 alkenes were obtained at 450 °C over the optimized catalyst, which is superior to all the previously reported carbon catalysts and shows a great potential for industrial application.

Methylation of Polyols with Trimethylphosphate in the Presence of a Lewis or Brønsted Acid Catalyst

M.-C. Duclos, A. Herbinski, A.-S. Mora, E. Métay, M. Lemaire,
ChemSusChem 2018, 11, 547

The alkylation of alcohols and polyols has been investigated with alkylphosphates in the presence of a Lewis or Brønsted acid catalyst. The permethylation of polyols was developed under solvent-free conditions at 100 °C with either iron triflate or Aquivion PW98, affording the isolated products in yields between 52 and 95 %. The methodology was also adjusted to carry out peralkylation with longer alkyl chains.
Kinematic Modeling of Mechanocatalytic Depolymerization of α-Cellulose and Beechwood

M. Kessler, R. T. Woodward, N. Wong, R. Rinaldi


Mechanocatalytic depolymerization of lignocellulose presents a promising method for the solid-state transformation of acidified raw biomass into water-soluble products (WSPs). However, the mechanisms underlining the utilization of mechanical forces in the depolymerization are poorly understood. A kinematic model of the milling process is applied to assess the energy dose transferred to cellulose during its mechanocatalytic depolymerization under varied conditions (rotational speed, milling time, ball size, and substrate loading). The data set is compared to the apparent energy dose calculated from the kinematic model and reveals key features of the mechanocatalytic process. At low energy doses, a rapid rise in the WSP yield associated with the apparent energy dose is observed. However, at a higher energy dose obtained by extended milling duration or high milling speeds, the formation of a substrate cake layer on the mill vials appear to buffer the mechanical forces, preventing full cellulose conversion into WSPs. By contrast, for beechwood, there exists a good linear dependence between the WSP yield and the energy dose provided to the substrate over the entire range of WSP yields. As the formation of a substrate cake in depolymerization of beechwood is less severe than that for the cellulose experiments, the current results verify the hypothesis regarding the negative effect of a substrate layer formed on the mill vials upon the depolymerization process. Overall, the current findings provide valuable insight into relationships between the energy dose and the extent of cellulose depolymerization effected by the mechanocatalytic process.
Maleic anhydride (MA_nh) and its acids are critical intermediates in chemical industry. The synthesis of maleic anhydride from renewable furfural is one of the most sought after processes in the field of sustainable chemistry. In this study, a plate vanadium phosphorus oxide (VPO) catalyst synthesized by a hydrothermal method with glucose as a green reducing agent catalyzes furfural oxidation to MA_nh in the gas phase. The plate catalyst—denoted as VPO_HT—has a preferentially exposed (200) crystal plane and exhibited dramatically enhanced activity, selectivity and stability as compared to conventional VPO catalysts and other state-of-the-art catalytic systems. At 360 °C reaction temperature with air as an oxidant, about 90 % yield of MA_nh was obtained at 10 vol % of furfural in the feed, a furfural concentration value that is much higher than those (<2 vol %) reported for other catalytic systems. The catalyst showed good long-term stability and there was no decrease in activity or selectivity for MA_nh during the time-on-stream of 25 h. The high efficiency and catalyst stability indicate the great potential of this system for the synthesis of maleic anhydride from renewable furfural.
Temperature Tuning the Catalytic Reactivity of Cu-Doped Porous Metal Oxides with Lignin Models

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Reported are the temperature dependencies of the temporal product evolution for lignin model compounds over copper-doped porous metal oxide (CuPMO) in supercritical-methanol (sc-MeOH). These studies investigated 1-phenylethanol (PPE), benzyl phenyl ether (BPE), dihydrobenzofuran (DHBF), and phenol over operating temperature ranges from 280 to 330 °C. The first three model compounds represent the β-O-4 and α-O-4 linkages in lignin as well as the furan group commonly found in the β-5 linkage. Phenol was investigated due to its key role in product proliferation as noted in earlier studies with this Earth-abundant catalyst. In general, the apparent activation energies for ether hydrogenolysis proved to be significantly lower than that for phenol hydrogenation, a major side reaction leading to product proliferation. Thus, temperature tuning is a promising strategy to preserve product aromaticity as demonstrated by the more selective conversion of BPE and PPE at lower temperatures. Rates of methanol reforming over CuPMO were also studied over the temperature range of 280–320 °C since it is this process that generates the reducing equivalents for this catalytic system. In the absence of substrate, the gaseous products H2, CO, and CO2 were formed in ratios stoichiometrically consistent with catalyzed methanol reformation and water gas shift reactions. The latter studies suggest that the H2 production ceases to be rate limiting early in batch reactor experiments but also suggest that H2 overproduction may contribute to product proliferation.
Enhancing Antioxidant Performance of Lignin by Enzymatic Treatment with Laccase

Zhili Li, Jiubing Zhang, Li Qin, and Yuanyuan Ge

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The utilization of lignin is of high interest since it represents the most abundant polyphenol worldwide. For the application of lignin as a natural antioxidant more phenolic hydroxyl groups (\(\text{Ph–OH}\)) and lower molecular weight (Mw) are essential. Here, we proposed a green method based on enzymatic treatment of two lignins (alkaline lignin AL and hydrolysis lignin HL) with laccase, by which the structure, especially the Ph–OH contents and Mw of lignin, could be effectively controlled. The antioxidant activity of the lignin was evaluated in vitro by DPPH• (1,1-diphenyl-2-picrylhydrazyl) radical scavenging ability. The mechanism of antioxidant activity improvement was also elucidated. As expected, the enzymatic treated lignin (HL-L1.0) with the highest Ph–OH content and lower Mw exhibited the strongest antioxidant activity (IC50 = 28.8 μg/mL), which was even stronger than the commercial antioxidants BHT (3,5-di-tert-butyl-4-hydroxytoluene, IC50 = 38.2 μg/mL) and BHA (3-tert-butyl-4-hydroxyanisole, IC50 = 56.3 μg/mL). This study suggested that the enzymatic treatment was a green and effective way to obtain lignin derivatives that showed great potential for antioxidant applications.

Trialkylamine-Catalyzed Aldolization of Unprotected 1,3-Dihydroxyacetone (DHA) toward C–C Bond-Linked Tetraol Surfactants

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The aldolization of unprotected 1,3-dihydroxyacetone (DHA) was studied under mild conditions (20 °C) in a mixture of water/EtOH using hydrocinnamaldehyde as a model substrate. It was shown that trimethylamine is the most effective base for this transformation, giving the corresponding aldol with up to 98% selectivity and 82% yield. The method was extended to a range of (biobased) aldehydes to give \(\alpha\)-hydroxyketones with 29–70% isolated yields. These \(\alpha\)-hydroxyketones were reduced under hydrogen using 5%-Ru/Al2O3 in EtOH at 100 °C to give tetraols with 79–97% isolated yields. The physicochemical properties of these tetraols were studied (CMC, Krafft point, PIT-slope method), and these studies revealed that this new class of C–C bond-linked nonionic surfactants exhibits high effectiveness, reducing the surface tension of water.
The role of substituents in the acidolysis of several lignin models bearing a β-O-4 linkage was studied through experimental (by using Nafion SAC-13 as a heterogeneous catalyst) and theoretical data (including transition state calculations). An equilibrium involving the protonation of either α-OH or β-OH groups as well as the dehydration of the α-OH protonated form to yield a benzylic carbocation is assumed. Phenylacetaldehyde and phenol derivatives are the major reaction products for a number of lignin models, though other products have also been identified (such as enol ethers and coumaran derivatives). The high reactivity observed for lignin models bearing an ortho-methoxy group on the O-bound phenyl ring has been attributed to the methoxy anchimeric assistance to the benzylic position. On the other hand, the low formaldehyde yields observed in the acidolysis of some lignin models have been attributed to the hydrogen bond formation between the hydroxymethyl group and the base abstracting the β- hydrogen of the carbocationic intermediate.
We modified lignin, a renewable biomacromolecule with high carbon density, with silicon-containing vinyl groups via a highly efficient silylation reaction that achieved ~30% substitution of lignin’s hydroxyl units. This exothermic process was carried out in the melt state, in situ, in a reactive extruder. 1H, 13C, and 31P NMR and FTIR confirmed the success of the silylation and were used to access the reactivity of the vinyl silylated lignin for copolymerization with polyacrylonitrile (PAN). Copolymers of the unmodified lignin and PAN were also produced as a reference. Importantly, the rheological behaviors of the copolymers of lignin and PAN were suitable for application in surface coating and films that were not possible if lignin or physical mixtures of lignin and PAN were used. Glass surfaces were treated via solution casting followed by oven drying, yielding films that were evaluated regarding their morphology (SEM) and thermal properties (TGA and DSC). The films produced with copolymers based on vinyl silylated lignin displayed a Young modulus of 486 MPa, an ultimate stress of 18 MPa, and a strain of 55% (DMA). These results indicate a much tougher system than that achieved after copolymerization of the unmodified lignin with PAN (ultimate stress and strain of less than 10 MPa and 10%, respectively). Overall, the introduced SiC and SiOC bonds improved lignin macromolecular mobility and facilitated its processability due to the remarkably low viscosity of the system. Our results show promising opportunities for lignin utilization as a precursor of copolymers, as illustrated here with PAN, for the synthesis of flexible films and other advanced materials.
Laccase/Mediator Systems: Their Reactivity toward Phenolic Lignin Structures

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Laccase-mediator systems (LMS) have been widely studied for their capacity to oxidize the nonphenolic subunits of lignin (70–90% of the polymer). The phenolic subunits (10–30% of the polymer), which can also be oxidized without mediators, have received considerably less attention. Consequently, it remains unclear to what extent the presence of a mediator influences the reactions of the phenolic subunits of lignin. To get more insight in this, UHPLC-MS was used to study the reactions of a phenolic lignin dimer (GBG), initiated by a laccase from Trametes versicolor, alone or in combination with the mediators HBT and ABTS. The role of HBT was negligible, as its oxidation by laccase occurred slowly in comparison to that of GBG. Laccase and laccase/HBT oxidized GBG at a comparable rate, resulting in extensive polymerization of GBG. In contrast, laccase/ABTS converted GBG at a higher rate, as GBG was oxidized both directly by laccase but also by ABTS radical cations, which were rapidly formed by laccase. The laccase/ABTS system resulted in Cα oxidation of GBG and coupling of ABTS to GBG, rather than polymerization of GBG. Based on these results, we propose reaction pathways of phenolic lignin model compounds with laccase/HBT and laccase/ABTS.
Significance of Lignin S/G Ratio in Biomass Recalcitrance of Populus trichocarpa Variants for Bioethanol Production

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Lignin S/G ratio has been investigated as an important factor in biomass recalcitrance to bioethanol production. Because of the complexity and variety of biomass, recalcitrance was also reportedly influenced by several other factors, such as total lignin content, degree of cellulose polymerization, etc. In addition, the effect of S/G ratio on biomass conversion is not uniform across plant species. Herein, 11 Populus trichocarpa natural variants grown under the same conditions with similar total lignin content were selected to minimize the effects of other factors. The lignin S/G ratio of the selected P. trichocarpa natural variants showed negative correlations with p-hydroxybenzoate (PB) and β–5 linkage contents, while it had positive ones with β-O-4 linkage, lignin molecular weight, and ethanol production. This study showed the importance of lignin S/G ratio as an independent recalcitrance factor that may aid future energy crop engineering and biomass conversion strategies.

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In this work, biobased hydrogels with temperature and pH responsive properties were prepared by copolymerizing N-isopropylacrylamide (NIPAM), itaconic acid (IA), and methacrylated lignosulfonate (MLS), where the multifunctional MLS served as a novel macro-cross-linker. The network structures of the lignosulfonate-NIPAM-IA hydrogels (LNIH) were characterized and confirmed by elemental analysis, Fourier transform infrared, and 13C nuclear magnetic resonance. The equilibrium swelling capacity of the LNIH hydrogel decreased from 31.6 to 19.1 g/g with MLS content increasing from 3.7 to 14.3%, suggesting a strong dependence of water absorption of the gel on MLS content. LNIH hydrogels showed temperature-sensitive behaviors with volume phase transition temperature (VPTT) around the body temperature, which was also influenced by MLS content. Moreover, all LNIH hydrogels exhibited pH sensitivity in the range of pH 3.0 to 9.1. Rheological study indicated that mechanical strength of the gel also increased with MLS content. The results from this study suggest that lignosulfonate derivative MLS is a potential feedstock serving both water-absorbing moiety and cross-linker for preparation of biobased smart hydrogels.
Ruthenium Nanoparticle-Decorated Porous Organic Network for Direct Hydrodeoxygenation of Long-Chain Fatty Acids to Alkanes

Sujan Mondal, Ramana Singuru, Subhash Chandra Shit, Taku Hayashi, Stephan Irle, Yuh Hijikata, John Mondal, and Asim Bhaumik

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With the rapidly diminishing fossil fuel resources, development of a new strategy for synthesis of biofuels from renewable resources can provide a sustainable alternative to our energy demand. We present the design, synthesis, and characterization of a new porous organic network (TpPON) through acid-catalyzed condensation of 1,3,5-triformylphloroglucinol (Tp) and triphenylamine (TPA). Ru0 nanoparticles are successfully fabricated at the porous surface of TpPON to obtain a novel catalytic system Ru@TpPON, which exhibits excellent catalytic performance together with outstanding stability for the hydrodeoxygenation of various vegetable oils to long-chain alkanes in water, and thus TpPON has wide potential for large-scale biodiesel production from renewable resources.
Palladium-catalyzed hydroformylation of terminal arylacetylenes with glyoxylic acid

Yang Liu, Liangzhen Cai, Sheng Xu, Weiwen Pu and Xiaochun Tao


A simple, practical and governable palladium-catalyzed hydroformylation of terminal arylacetylenes has been disclosed. The reaction proceeds under syngas-free conditions, using readily available glyoxylic acid as the formyl source, under mild conditions, giving rise to a broad range of α,β-unsaturated aldehydes.

Nickel-catalyzed C–O bond reduction of aryl and benzyl 2-pyridyl ethers

Jing Li and Zhong-Xia Wang


The reduction of aryl and benzyl 2-pyridyl ethers with sodium isopropoxide was carried out via nickel-catalyzed C–OPy bond cleavage, giving reductive products in reasonable to excellent yields. This method allowed the 2-pyridyloxy group to be directly removed with high efficiency, mild reaction conditions, and good compatibility of functional groups.

A strategy for generating aryl radicals from arylborates through organic photoredox catalysis: photo-Meerwein type arylation of electron-deficient alkenes

Y. Iwata, Y. Tanaka, S. Kubosaki, T. Morita and Y. Yoshimi


Photoinduced reactions of arylboronic acids with electron deficient alkenes under mild organic photoredox catalysis conditions lead to the formation of Meerwein arylation type adducts via the generation of aryl radicals.
Controllable assembly of the benzothiazole framework using a C≡C triple bond as a one-carbon synthon

Yubing Huang, Donghao Yan, Xu Wang, Peiqi Zhou, Wanqing Wu and Huanfeng Jiang

*Chem. Commun.*, 2018, 54, 1742–1745

A concise and efficient protocol to assemble diverse benzothiazole derivatives in high yields was provided via copper catalyzed tandem cyclization with o-haloanilines, elemental sulfur and terminal alkynes as raw materials. In this protocol, C atoms on the C≡C triple bond were controllably involved in the construction of the benzothiazole framework and multiple carbon–heteroatom bonds through divergent routes.

\[(\text{Ge}_2\text{P}_2)^{2-} : \text{a binary analogue of P}_4 \text{ as a precursor to the ternary cluster anion } \text{[Cd}_3(\text{Ge}_3\text{P})_3]^{3-}\]

Stefan Mitzinger, Jascha Bandemehr, Kevin Reiter, J. Scott McIndoe, Xiulan Xie, Florian Weigend, John F. Corrigan and Stefanie Dehnen

*Chem. Commun.*, 2018, 54, 1421–1424

The novel binary P₄ analogue (Ge₂P₂)²⁻ proved to be a suitable precursor for heteroatomic cluster synthesis. Over time in solution, it rearranges to form (Ge₇P₂)²⁻, as shown by NMR studies and X-ray diffraction. Reactions of (Ge₂P₂)²⁻ with CdPh₂ afford [K(crypt-222)]₃[Cd₃(Ge₃P)₃], containing an unprecedented ternary cluster anion with a triangular Cd₃ moiety.
Two efficient pathways for the synthesis of aryl ketones catalyzed by phosphorus-free palladium catalysts

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*Molecular Catalysis, 2018, 445, 61–72*

Allylic alcohols, 1-buten-3-ol, 1-penten-3-ol and 1-octen-3-ol, reacted with aryl iodides (iodotoluene, 4-iodotoluene, 4-iodophenol and 4-iodanisole) under Heck reaction conditions to form corresponding saturated aryl ketones in one step. The same products were obtained in a two-step tandem reaction consisted of the Heck coupling of allylic alcohols with aryl iodides, followed by hydrogenation. Reactions were catalyzed by phosphorus-free palladium precursors modified with the menthol-substituted imidazolium chlorides. Formation of crystalline palladium nanoparticles, of the diameter up to 65 nm, in the reaction mixture was evidenced by TEM.

Hydrogenolysis of lignin model compounds into aromatics with bimetallic Ru-Ni supported onto nitrogen-doped activated carbon catalyst

Yinghui Hu, Guangce Jiang, Guoqiang Xu, Xindong Mu

*Molecular Catalysis, 2018, 445, 316–326*

Lignin is the most abundant and renewable resources for production of natural aromatics. In this paper, new bimetallic catalytic system of Ru and Ni supported onto nitrogen-doped activated carbon (Ru-Ni-AC/N) was developed and its performances on hydrogenolysis of lignin model compounds under mild reaction conditions (1.0 MPa, 230 °C, in aqueous) were investigated. The results indicate that Ru-Ni-AC/N was a highly active, selective and stable catalyst for the conversion of lignin model compounds into aromatics, e.g. phenol, benzene and their derivatives. As verified by BET, XRD, HRTEM, XPS, H₂-TPR and ICP-MS, the strong synergistic effects between i) Ru and Ni and ii) metals and N-groups were contributed to its excellent aromatics selectivity. What’s more, the introduction of electron rich N atoms on AC was beneficial to the stabilization of metal particles, which greatly enhanced the durability of the catalyst.
H₂ photo-production from methanol, ethanol and 2-propanol: Pt-(Nb)TiO₂ performance under UV and visible light

Olga Fontelles-Carceller, Mario J. Munoz-Batista, José Carlos Conesa, Anna Kubacka, Marcos Fernández-Garcia

Molecular Catalysis 2018, 446, 88–97

In this work we analyzed the photo-production of hydrogen using titania-based systems able to profit from UV and visible light photons. For this purpose, we prepared Niobium-doped titania and a titania reference by a microemulsion method, subjected these oxide precursors to calcination and subsequently introduced Pt as co-catalyst by a chemical reduction method. These materials were characterized in terms of the structural and morphological properties of the oxide and metal phases. Using these materials, we measured the reaction rate and quantum efficiency of the hydrogen photo-production using methanol, ethanol, and 2-propanol as sacrificial agents. Significant activity enhancement was observed in the Niobium-doped material with respect to the titania reference material. The study focuses on interpreting the differences presented (between the two samples) among the three alcohols in the hydrogen yield and provides a physico-chemical study to understand the roots of the activity. Such study was mainly based on the analysis of the reaction mechanism using in-situ infrared spectroscopy together with the analysis of the energetics of the reaction taking into account the fate of the sacrificial alcohol during reaction.

Hydrogenolysis of sorbitol into valuable C3-C2 alcohols at low H₂ pressure promoted by the heterogeneous Pd/Fe₃O₄ catalyst

Bianca Gumina, Francesco Mauriello, Rosario Pietropaolo, Signorino Galvagno, Claudia Espro

Molecular Catalysis, 2018, 46, 152–160

The hydrogenolysis of sorbitol and various C5-C3 polyols (xylitol; erythritol; 1,2- 1,4- and 2,3-butandiol; 1,2-propandiol; glycerol) have been investigated at low molecular hydrogen pressure (5 bar) by using Pd/Fe₃O₄, as heterogeneous catalyst and water as the reaction medium. Catalytic experiments show that the carbon chain of polyols is initially shortened through dehydrogenation/decarbonylation and dehydrogenation/retro-aldol mechanisms followed by a series of cascade reactions that include dehydrogenation/decarbonylation and dehydration/hydrogenation processes. At 240 °C, sorbitol is fully converted into lower alcohols with ethanol being the main reaction product in liquid phase.
Alternative Sm(II) Species-Mediated Cascade Coupling/Cyclization for the Synthesis of Oxobicyclo[3.1.0]hexane-1-ols
Bingxin You, Mengmeng Shen, Guanqun Xie, Hui Mao, Xin Lv, and Xiaoxia Wang

The allylSmBr/HMPA/MsOH system has been found to be an efficient reagent for the “ester-alkene” coupling/cyclization cascade of readily available α-allyloxy esters. Oxobicyclo[3.1.0]hexane-1-ols were thus prepared in good to excellent yields and diastereoselectivities. Investigation on the mechanism suggested the possible existence of a new Sm(II) species, namely, CH$_3$SO$_3$SmBr, which resulted from the reaction between allylSmBr and MsOH and may be the actual SET reagent.

Flow Photochemistry as a Tool for the Total Synthesis of (++)-Epigalcatin
Kamil Lisiecki and Zbigniew Czarnocki
*Org. Lett.*, 2018, 20(3), 605

The first total synthesis of (++)-epigalcatin was completed in a highly stereoselective manner starting from piperonal, 3,4-dimethylbenzaldehyde, and diethyl succinate. l-Prolinol was used as a chiral auxiliary. The crucial step in this procedure involves the construction of the cyclolignan framework by continuous-flow photocyclization of a chiral atropisomeric 1,2-bisbenzylidenesuccinate amide ester.

Synthesis and Reaction of ortho-Benzquinone Monohemiaminals
Wenfang Xiong, Donghao Emi Saito, Yuri Matsumoto, Akihiko Nakamura, Yuki Namera, and Masahisa Nakada

The preparation and reactions of ortho-benzquinone monohemiaminals are described. The oxidative dearomatization of phenols bearing amino alcohol groups induced N-cyclization to afford ortho-benzquinone monohemiaminals. The N-cyclization stereoselectively affords the product when a chiral amino alcohol is used as the substituent. The chiral ortho-benzquinone monohemiaminal undergoes stereoselective Diels–Alder reactions with electron-deficient alkenes, as expected, confirming the promising utility of ortho-benzquinone monohemiaminals.

Photocatalytic and Chemoselective Transfer Hydrogenation of Diarylimines in Batch and Continuous Flow
Dean J. van As, Timothy U. Connell, Martin Brzozowski, Andrew D. Scully, and Anastasios Polyzos

A visible-light photocatalytic method for the chemoselective transfer hydrogenation of imines in batch and continuous flow is described. The reaction utilizes Et$_3$N as both hydrogen source and single-electron donor, enabling the selective reduction of imines derived from diarylketimines containing other reducible functional groups including nitriles, halides, esters, and ketones. The dual role of Et$_3$N was confirmed by fluorescence quenching measurements, transient absorption spectroscopy, and deuterium-labeling studies. Continuous-flow processing facilitates straightforward scale-up of the reaction.
Copper-Catalyzed Fluoroolefination of Silyl Enol Ethers and Ketones toward the Synthesis of β-Fluoroenones
Yanlin Li, Jing Liu, Shuang Zhao, Xuzhao Du, Minjie Guo, Wentao Zhao, Xiangyang Tang, and Guangwei Wang

A general and facile synthetic method for β-fluoroenones from silyl enol ethers or ketones, with a copper–amine catalyst system, has been developed. The reaction proceeded by a tandem process of difluoroalkylation–hydrolysis–dehydrofluorination. This method is characterized by high yields, excellent Z/E ratios, a low-cost catalyst, and a broad substrate scope. The synthetic potential of β-fluoroenones has been demonstrated by the construction of various complicated organofluorine molecules.

Enantioselective Trapping of Oxonium Ylides by 3-Hydroxyisoindolinones via a Formal S_N1 Pathway for Construction of Contiguous Quaternary Stereocenters
Zhenghui Kang, Dan Zhang, Jiayi Shou, and Wenhao Hu

An enantioselective Rh(II)/chiral phosphoric acid co-catalyzed three-component reaction via trapping of oxonium ylides with 3-hydroxyisoindolinones by a formal S_N1 pathway is described. This reaction allows for the efficient synthesis of isoindolinone derivatives with two contiguous quaternary stereogenic centers in high yields (up to 93%) with excellent enantioselectivities and moderate diastereoselectivities under mild reaction conditions.

Photoinduced Multicomponent Synthesis of α-Silyloxy Acrylamides, an Unexplored Class of Silyl Enol Ethers
Francesco Ibba, Pietro Capurro, Silvia Garbarino, Manuel Anselmo, Lisa Moni, and Andrea Basso

The photoinduced, multicomponent reaction of α-diazoketones, silanols, and isocyanides affords α-silyloxy acrylamides, formally derived from α-keto amides. The presence of a secondary amido group makes classic preparative methods for silyl enol ethers unfeasible in this case, while the mild conditions required by this photochemical approach allow their synthesis in good yields; moreover, the general structure can be easily modified by varying each component of the multicomponent reaction. Fine-tuning of the reaction conditions (i.e., solvents, radiation, additives) can be exploited to obtain complete Z selectivity. The reactivity of this overlooked class of silyl enol ethers has been investigated, and features that could pave the way to new applications have been found.
Fe(II)/Fe(III)-Catalyzed Intramolecular Didehydro-Diels–Alder Reaction of Styrene-ynes
Hyeon Jin Mun, Eun Young Seong, Kwang-Hyun Ahn, and Eun Joo Kang

*J. Org. Chem., 2018, 83 (3), 1196*

The intramolecular didehydro-Diels–Alder reaction of styrene-ynes was catalyzed by Fe(II) and Fe(III) to produce various naphthalene derivatives under microwave heating conditions. Mechanistic calculations found that the Fe(II) catalyst activates the styrenyl diene in an inverse-electron-demand Diels–Alder reaction, and the consecutive dehydrogenation reaction can be promoted by either Fe(II)-catalyzed direct dehydrogenation or an Fe(III)-catalyzed rearomatization/dehydrogenation pathway.

Tetiana Druzhenko, Yevhen Skalenko, Maryna Samolenko, Aleksandr Denisenko, Sergey Zozulya, Petro O. Borysko, Maria I. Sokolenko, Alexandr Tarasov, and Pavel K. Mykhailiuk

*J. Org. Chem., 2018, 83 (3), 1304*

Intramolecular photochemical [2 + 2]-cyclization of acetonophene enamides gave 2-azabicyclo[3.2.0]heptanes, advanced building blocks for drug discovery. Synthesis of a conformationally restricted analogue of proline, 2,3-ethanoproline, was performed.

Visible-Light-Mediated Decarboxylative Alkylation Cascade Cyano Insertion/Cyclization of N-Arylacrylamides under Transition-Metal-Free Conditions
Yulan Yu, Weiwen Yuan, Hansheng Huang, Zhiqiang Cai, Ping Liu, and Peipei Sun

*J. Org. Chem., 2018, 83 (3), 1654*

The visible-light-mediated decarboxylative functionalization of aliphatic carboxylic acids using organocatalysts has rarely been reported. This study represented an environmentally benign decarboxylation method involving the combination of eosin Y and (NH₄)₂S₂O₈. This system converted aliphatic carboxylic acids to alkyl radicals, followed by their addition to the carbon–carbon double bond of the N-arylacrylamide cascade cyano insertion/cyclization to construct alkylated phenanthridines in moderate to good yields under photoredox catalysis.

Weak Directing Group Steered Formal Oxidative [2+2+2]-Cyclization for Selective Benzannulation of Indoles
Kiran R. Bettadapur, Raja Kapanaiah, Veeranjaneyulu Lanke, and Kandikere Ramaiah Prabhu

*J. Org. Chem., 2018, 83 (4), 1810*

A double C–H activation and double insertion process to achieve the synthesis benzo[e]indole frameworks has been disclosed. This type of benzannulation is directed by a trifluoromethylketone moiety, which is easy to install on the indole C3-position. Overall the reaction takes places as an oxidative cyclization of two alkynes with the C4–C5 position of indole.
Photochemically Induced Intramolecular Radical Cyclization Reactions with Imines
Corentin Lefebvre, Clément Michelin, Thomas Martzel, Vanek Djou'ou Mvondo, Véronique Bulach, Manabu Abe, and Norbert Hoffmann

The photochemically induced intramolecular hydrogen abstraction or hydrogen atom transfer in cyclic imines 8a,b followed by a cyclization is investigated. Two types of products are observed, one resulting from the formation of a C–C bond, the other from the formation of a C–N bond. A computational study reveals that hydrogen is exclusively transferred to the imine nitrogen leading to a triplet diradical intermediate. After intersystem crossing, the resulting zwitterionic intermediate undergoes cyclization leading to the final product.

Enantioselective Dearomatization of Alkylpyridiniums by N-Heterocyclic Carbene-Catalyzed Nucleophilic Acylation
Graziano Di Carmine, Daniele Ragno, Olga Bortolini, Pier Paolo Giovannini, Andrea Mazzanti, Alessandro Massi, and Marco Fogagnolo

A chiral NHC-catalyzed dearomatizing reaction of activated N-alkylpyridinium salts with aliphatic aldehydes is described. The resulting acylated 1,4-dihydropyridines have been obtained with complete C4 regioselectivity and enantioselectivities in the range 52–78% ee. The (4R)-absolute configuration of the synthesized compounds has been determined by the TD-DFT simulation of the electronic circular dichroism spectra.

Acid/Base-Co-catalyzed Direct Oxidative α-Amination of Cyclic Ketones: Using Molecular Oxygen as the Oxidant
Yi-Jin Li, Lu Zhang, Na Yan, Xiang-He Meng, Yu-Long Zhao

A novel acid/base-co-catalyzed direct intermolecular α-amination of various cyclic ketones has been developed for the first time. The reaction employs molecular oxygen as the sole oxidant under metal-free conditions. The reaction tolerates a wide range of various anilines, especially primary diamine derivatives, and provides a simple and efficient method for the constructions of α-amino enones and benzodiazepine derivatives in a single step.
Direct ortho-Acylxylation of Arenes and Alkenes by Cobalt Catalysis
Cong Lin, Zhengkai Chen, Zhanxiang Liu, Yuhong Zhang

An efficient protocol for the cobalt-catalyzed acyloxylation of arenes and alkenes with the assistance of an 8-aminoquinolyl auxiliary group is reported. In this transformation, benzoic acids, alkenyl acids, and aliphatic acids could be readily involved to afford structurally diverse esters. It is worth noting that the silver sulfate (Ag2SO4) oxidant is renewable and the directing group could be removed and recycled. The strategy represents the first successful example of transition metal-catalyzed acyloxylation of alkenyl carboxamides C(sp2)−H bonds with carboxylic acids.

Photocatalytic Oxidative Bromination of Electron-Rich Arenes and Heteroarenes by Anthraquinone
Daniel Petzold, Burkhard König

The estimated excited oxidation potential of sodium anthraquinone-2-sulfonate (SAS) increases from 1.8 V to about 2.3 V vs SCE by protonation with Brønsted acids. This increased photooxidation power of protonated anthraquinone was used for the regio-selective oxidative bromination of electron rich (hetero)arenes and drugs in good yield. The mild reaction conditions are compatible with many functional groups, such as double and triple bonds, ketones, amides and amines, hydroxyl groups, carboxylic acids and carbamates. Mechanistic investigations indicate the photooxidation of the arene followed by nucleophilic bromide addition as the likely pathway.

Chiral Phosphoric Acid Catalyzed Enantioselective Friedel-Crafts Reaction of N-Protected 4-Aminoindoles with β,γ-Unsaturated α-Ketimino Esters
Yu-Yang Ding, Deng-Feng Xu, Shan-Shui Meng, Yang Li, Jun-Ling Zhao

Through a hydrogen bonding guided substrate modification strategy, we have developed a chiral phosphoric acid catalyzed highly enantioselective Friedel-Crafts reaction of N-protected 4-aminoindoles with β,γ-unsaturated α-ketimino esters. The mechanism and origins of the enantioselectivity of this process are indentified using DFT calculations. Both the experimental and calculation results indicated that the NH moiety at the indole C4 position is essential for the stereocontrol of this reaction. To further examine the potential usefulness of this method, gram scale synthesis and derivatizations of one of the products were also carried out.
Ruthenium(II)-NNN-Pincer-Complex-Catalyzed Reactions Between Various Alcohols and Amines for Sustainable C-N and C-C Bond Formation
Milan Maji, Kaushik Chakrabarti, Bhaskar Paul, Bivas Chandra Roy, Sabuj Kundu

An air and moisture stable 2-hydroxypyridine based bifunctional ruthenium NNN-pincer complex catalyzed efficient (TON=42840) N-alkylation of amines under mild conditions. Surprisingly, with cyclic secondary amines this methodology selectively produced only amides. Notably, N-methylation of several amines was achieved by using methanol as a green methylating agent. Furthermore, with lower catalyst loading (0.2 mol%) and shorter reaction time (6 h) numerous substituted quinolines were synthesized from 2-aminobenzyl alcohols and secondary alcohols. The effectiveness of this protocol was further extended by successfully synthesizing 2-alkylaminoquinolines in a one-pot fashion from amino alcohol, aliphatic nitriles, and alcohols. Gram scale synthesis of various compounds was also investigated to demonstrate the synthetic applicability of this methodology.

Ligand-free Iron(II)-Catalyzed N-Alkylation of Hindered Secondary Arylamines with Non-activated Secondary and Primary Alcohols via a Carbocationic Pathway
Onkar S. Nayal, Maheshwar S. Thakur, Manoranjan Kumar, Neeraj Kumar, Sushil K. Maurya

Secondary benzylic alcohols represent a challenging class of substrates for N-alkylation of amines. Herein, we describe an iron(II)-catalyzed eco-friendly protocol for N-alkylation of secondary arylamines with secondary benzylic alcohols through a carbocationic pathway instead of the known borrowing hydrogen transfer (BHT) approach. Transiently generated carbocations, produced from alcohols via self-condensation, were coupled with arylamines to provide highly functionalized amine products. The scope of this methodology involves N-alkylation of primary, secondary and heterocyclic amines with primary/secondary benzylic, allylic and heterocyclic alcohols, which are common key structures in numerous pharmaceuticals drugs. The method can also be easily adopted for the amination of various natural products.
A mechanistic approach towards the photocatalytic organic transformations over functionalised metal organic frameworks: a review
Satyabrata Subudhi, Dharitri Rath and K. M. Parida
Catalysis Science & Technology, 2018, 8, 679-696

Photocatalytic organic transformations driven by functionalised metal organic frameworks (MOFs) are a green perspective for fine chemical synthesis. In the class of highly porous materials, MOFs are unparalleled in their degree of tunability and structural diversity and range of physical and chemical properties such as large surface area, permanent porosity, large void volumes, and framework flexibility, because of which they can act as a sustainable alternative for inorganic semiconductors. MOFs are the latest class of ordered porous solids being intensively studied as a novel class of hybrid organic–inorganic materials as nanophotocatalysts in the field of chemistry, materials science, chemical engineering, etc. Although the photocatalytic application of MOFs is still in the early stages compared with their other applications such as gas storage, separation, and heterogeneous catalysis, the currently available results have revealed that functionalised MOFs are very active as photocatalysts. The present review aims to discuss the various synthetic methods, post-synthetic modifications, MOF catalysed organic reactions and proposed mechanistic pathways for photoinduced organic transformations.

Visible light-driven selective hydrogenation of unsaturated aromatics in an aqueous solution by direct photocatalysis of Au nanoparticles
Yiming Huang, Zhe Liu, Guoping Gao, Qi Xiao, Wayde Martens, Aijun Du, Sarina Sarina, Cheng Guo and Huaiyong Zhu
Catalysis Science & Technology, 2018, 8, 726-734

Selective hydrogenation of various chemical bonds, such as C=C, C≡C, C=O, N=O, and C≡N, is efficiently driven by visible light over a supported gold nanoparticle (AuNP) photocatalyst under mild reaction conditions. The reaction system exhibits high substituent tolerance and tunable selectivity by light wavelength. Density functional theory (DFT) calculations demonstrated a strong chemisorption between the reactant molecule and metal resulting in hybridized orbitals. It is proposed that direct photoexcitation between hybridized orbitals is the main driving force of the hydrogenation reaction. The hydrogenation pathway is investigated by the isotope tracking technique. We revealed the cooperation of water and formic acid (FA) as a hydrogen source and the hydrogenation route through Au–H species on the AuNP surface.
Size-dependent catalytic performance of ruthenium nanoparticles in the hydrogenolysis of a β-O-4 lignin model compound

Lin Dong, Li-Li Yin, Qineng Xia, Xiaohui Liu, Xue-Qing Gong and Yanqin Wang

Catalysis Science & Technology, 2018, 8, 735-745

One-pot depolymerization of lignin to well-defined chemicals and their further deoxygenation to arenes are extremely attractive. Based on our previous results that Nb2O5 species can promote the cleavage of C–O bonds and the synergistic effect between Ru and Nb2O5 species led to the direct transformation of lignin into arenes over a Ru/Nb2O5 catalyst [Nat. Commun., 2017, 8, 161041], the importance and influence of ruthenium particle size need to be further studied. Herein, we report the different performances of Ru/NbOPO4 catalysts with various Ru particle sizes in the hydrogenolysis of a lignin model compound. This study shows that the catalytic activities and the product distributions strongly depend on the size of Ru nanoparticles (NPs): Ru NPs with smaller diameters (1.2 and 1.8 nm) have a higher activity for the cleavage of Caryl–O and Caromatic–O bonds, whereas Ru NPs with larger diameters (2.5 and 5.3 nm) show a much lower activity for C–O cleavage, especially for the Caromatic–O bond, resulting in totally different product distributions. Density functional theory (DFT) calculations revealed that the presence of step and edge sites in smaller Ru particles can significantly lower the barriers for both Caromatic–O and Caryl–O bond cleavage. This study provides a new way for catalyst design towards highly efficient and selective hydrogenolysis of lignin to useful aromatic chemicals.

Magnetic nickel ferrite nanoparticles as highly durable catalysts for catalytic transfer hydrogenation of bio-based aldehydes

Jian He, Song Yang and Anders Riisager

Catalysis Science & Technology, 2018, 8, 790-797

Magnetic nickel ferrite (NiFe2O4) nanoparticles were exploited as stable and easily separable heterogeneous catalysts for catalytic transfer hydrogenation (CTH) of furfural to furfuryl alcohol with 2-propanol as both the hydrogen source and the solvent providing 94% product yield at 180 °C after 6 h of reaction. The magnetic properties of the catalysts provided facile recovery using an external magnet after reaction allowing it to be reused in five reaction cycles without loss of catalytic performance. Importantly, the NiFe2O4 nanoparticles were also applicable to CTH of other alkenyl/allyl/aromatic aldehydes affording over 94% selectivity towards the targeted alcohol products, thus being attractive as highly universal catalysts for CTH of aldehydes.
Mechanistic study on –C–O– and –C–C– hydrogenolysis over Cu catalysts: identification of reaction pathways and key intermediates

Benjamin Kühne, Herbert Vogel, Reinhard Meusinger, Sebastian Kunz and Markwart Kunz

Catalysis Science & Technology, 2018, 8, 755-767

Important petro-based polyol compounds with a longer carbon chain, such as oligohydroxy hexanes (e.g. 1,2- and 1,6-hexanediol or 1,2,6-hexanetriol), require at least three to four synthesis steps. Replacing this complex chemistry by a one-pot reaction via –C–O– bond cleavage from sugars would be a significant breakthrough for the use of renewable feedstocks. Cu is known for its dehydroxylation (deoxygenation) properties, yielding the desired products from sugars. In this joint research between academic and industrial chemistry, we have identified so far unknown intermediate products and present the first mechanism that explains the selective cleavage of OH-groups over copper. Strong interactions between polyols, unsaturated species and the copper surface are observed. Stable five-membered rings are formed with Cu via two vicinal OH-groups of the polyol reactant that makes these OH-groups inert to –C–O– bond cleavage. Adjacent free OH-groups in close proximity to the catalyst are dehydroxylated (deoxygenated). We further show that degradation of polyols not only occurs via commonly cited retro-aldol reactions. The formation of acid intermediates with subsequent decarboxylation is validated as a new pathway for –C–C– bond cleavage to short-chain polyols and CO₂. The proposed mechanisms for –C–O– and –C–C– bond cleavage elucidate why hydrogenolysis reactions require high hydrogen pressure (up to 200 bar) to suppress the degradation of sugars and obtain high yields of deoxy C6 products. With this knowledge, the improvement of a standard commercial Cu-RANEY® catalyst under optimized reaction conditions was shown. In contrast to alumina-supported Cu, the Cu–Al alloy in a RANEY®-type catalyst shows selective –C–O– bond cleavage properties while maintaining the C6 carbon chain. These new insights into the transformation of sugars to value added commodities show the potential for new approaches in future biorefinery concepts.
Catalytic conversion of biomass-derived levulinic acid into alcohols over nanoporous Ru catalyst

Jinkun Lv, Zeming Rong, Liming Sun, Chengyun Liu, An-Hui Lu, Yue Wang and Jingping Qu

Catalysis Science & Technology, 2018, 8, 975-979

Several Ru-based catalysts were employed for the hydrogenation of levulinic acid and nanoporous Ru showed attractive catalytic performance for alcohols production. It was found that the total yield of 2-butanol and 2-pentanol was 78.8% and the yield of 1,4-pentadiol was 74.6%, respectively acquired at 140 °C and 100 °C using H₂O as the solvent. Thanks to its acid site and lattice plane, nanoporous Ru provided sites for activating the lactone group of GVL and C–C/C–O bonds of PDO.

Stability of Pd nanoparticles on carbon-coated supports under hydrothermal conditions

Jiajie Huo, Robert L. Johnson, Pu Duan, Hien N. Pham, Deyny Mendivelso-Perez, Emily A. Smith, Abhaya K. Datye, Klaus Schmidt-Rohr and Brent H. Shanks

Catalysis Science & Technology, 2018, 8, 1151-1160

Hydrothermal stability is one of the major challenges facing heterogeneous catalysis in biomass conversion to chemicals or fuels. Though carbon supports have shown better hydrothermal stability than common metal oxide supports like alumina and silica, improving the stability of metal nanoparticles supported on carbon still remains a challenge. In this work, carbon-coated SBA-15 (mesoporous silica) materials in which thin carbon overlayers were pyrolyzed at 300, 400, and 600 °C giving different surface chemistries, as quantitatively verified by ¹³C NMR and XPS. As the pyrolysis temperature increased, the carbon overlayer had fewer oxygen functional groups and more aromatic groups. After depositing Pd nanoparticles on the support, hydrothermal treatments and aqueous-phase furfural hydrogenation were used to test the catalyst stability. Better Pd dispersion and enhanced hydrothermal stability were observed when Pd was supported on the carbon-coated SBA-15 pyrolyzed at lower temperature.
Cobalt-catalyzed electrooxidative C-H/N-H [4+2] annulation with ethylene or ethyne

Shan Tang, Dan Wang, Yichang Liu, Li Zeng & Aiwen Lei

Nature Communications 9, 2018, 798

Ethylene and ethyne are among the simplest two-carbon building blocks. However, quite limited methods can be applied to incorporate ethylene or ethyne into fine chemicals. Here we demonstrate a cobalt-catalyzed dehydrogenative C–H/N–H [4+2] annulation of aryl/vinyl amides with ethylene or ethyne by using an electrochemical reaction protocol. Significantly, this work shows an example of electrochemical recycling of cobalt catalyst in oxidative C–H functionalization reactions, avoiding the use of external chemical oxidants and co-oxidants. The electrochemical method provides a reliable and safe way for incorporating gas-phase ethylene or ethyne into fine chemicals. High reaction efficiency and good functional group tolerance are observed under divided electrolytic conditions.

Retrosynthesis of multi-component metal–organic frameworks

Shuai Yuan, Jun-Sheng Qin, Jialuo Li, Lan Huang, Liang Feng, Yu Fang, Christina Lollar, Jiandong Pang, Liangliang Zhang, Di Sun, Ali Alsalme, Tahir Cagin & Hong-Cai Zhou

Nature Communications 9, 2018, 808

Crystal engineering of metal–organic frameworks (MOFs) has allowed the construction of complex structures at atomic precision, but has yet to reach the same level of sophistication as organic synthesis. The synthesis of complex MOFs with multiple organic and/or inorganic components is ultimately limited by the lack of control over framework assembly in one-pot reactions. Herein, we demonstrate that multi-component MOFs with unprecedented complexity can be constructed in a predictable and stepwise manner under simple kinetic guidance, which conceptually mimics the retrosynthetic approach utilized to construct complicated organic molecules. Four multi-component MOFs were synthesized by the subsequent incorporation of organic linkers and inorganic clusters into the cavity of a mesoporous MOF, each composed of up to three different metals and two different linkers. Furthermore, we demonstrated the utility of such a retrosynthetic design through the construction of a cooperative bimetallic catalytic system with two collaborative metal sites for three-component Strecker reactions.

Expedient syntheses of N-heterocycles via intermolecular amphoteric diamination of allenes

Zhishi Ye, Sarju Adhikari, Yu Xia & Mingji Dai

Nature Communications 9, 2018, 721

Saturated 1,4-diazo heterocycles including piperazines, 1,4-diazepanes, and 1,4-diazocanes, are highly important for therapeutic development, but their syntheses are often tedious. We describe here an amphoteric diamination strategy to unite readily available 1,2-, 1,3- or 1,4-diamine derivatives with electron-deficient allenes via a formal \([n+2]\) \((n = 4, 5, 6)\) cyclization mode to produce the corresponding 1,4-diazo heterocycles in just one step. This strategy features mild reaction conditions, high functional group tolerance, and scalability (gram scale). The reagents used are cheap and readily available and no transition metal catalysts are needed. More sophisticated products containing trifluoromethyl group or bicyclic ring systems can be accessed via a one-pot procedure as well. Our mechanistic studies support that formation of mono-iodinated or chlorinated diamine intermediates is important for the desired transformation and the commonly proposed chloride-iodide exchange process and a radical N–C bond formation is unlikely when the combination of NCS/KI is used.
Structural basis for DNMT3A-mediated de novo DNA methylation


Abstract

DNA methylation by de novo DNA methyltransferases 3A (DNMT3A) and 3B (DNMT3B) at cytosines is essential for genome regulation and development1,2. Dysregulation of this process is implicated in various diseases, notably cancer. However, the mechanisms underlying DNMT3 substrate recognition and enzymatic specificity remain elusive. Here we report a 2.65-Å crystal structure of the DNMT3A–DNMT3L–DNA complex in which two DNMT3A monomers simultaneously attack two cytosine–phosphate–guanine (CpG) dinucleotides, with the target sites separated by 14 base pairs within the same DNA duplex. The DNMT3A–DNA interaction involves a target recognition domain, a catalytic loop, and DNMT3A homodimeric interface. Arg836 of the target recognition domain makes crucial contacts with CpG, ensuring DNMT3A enzymatic preference towards CpG sites in cells. Haematological cancer-associated somatic mutations of the substrate-binding residues decrease DNMT3A activity, induce CpG hypomethylation, and promote transformation of haematopoietic cells. Together, our study reveals the mechanistic basis for DNMT3A-mediated DNA methylation and establishes its aetiological link to human disease.
Palladium-catalysed electrophilic aromatic C–H fluorination

Kumiko Yamamoto, Jiakun Li, Jeffrey A. O. Garber, Julian D. Rolfes, Gregory B. Boursalian, Jannik C. Borghs, Christophe Genicot, Jérôme Jacq, Maurice van Gastel, Frank Neese & Tobias Ritter

Nature 2018, 554, 511.

Abstract

Aryl fluorides are widely used in the pharmaceutical and agrochemical industries1,2, and recent advances have enabled their synthesis through the conversion of various functional groups. However, there is a lack of general methods for direct aromatic carbon–hydrogen (C–H) fluorination3. Conventional methods require the use of either strong fluorinating reagents, which are often unselective and difficult to handle, such as elemental fluorine, or less reactive reagents that attack only the most activated arenes, which reduces the substrate scope. A method for the direct fluorination of aromatic C–H bonds could facilitate access to fluorinated derivatives of functional molecules that would otherwise be difficult to produce. For example, drug candidates with improved properties, such as increased metabolic stability or better blood–brain-barrier penetration, may become available. Here we describe an approach to catalysis and the resulting development of an undirected, palladium-catalysed method for aromatic C–H fluorination using mild electrophilic fluorinating reagents. The reaction involves a mode of catalysis that is unusual in aromatic C–H functionalization because no organometallic intermediate is formed; instead, a reactive transition-metal-fluoride electrophile is generated catalytically for the fluorination of arenes that do not otherwise react with mild fluorinating reagents. The scope and functional-group tolerance of this reaction could provide access to functional fluorinated molecules in pharmaceutical and agrochemical development that would otherwise not be readily accessible.
**Volatile chemical products emerging as largest petrochemical source of urban organic emissions**


*Science* 2018, (359) 6377, 760.

**Abstract**

A gap in emission inventories of urban volatile organic compound (VOC) sources, which contribute to regional ozone and aerosol burdens, has increased as transportation emissions in the United States and Europe have declined rapidly. A detailed mass balance demonstrates that the use of volatile chemical products (VCPs)—including pesticides, coatings, printing inks, adhesives, cleaning agents, and personal care products—now constitutes half of fossil fuel VOC emissions in industrialized cities. The high fraction of VCP emissions is consistent with observed urban outdoor and indoor air measurements. We show that human exposure to carbonaceous aerosols of fossil origin is transitioning away from transportation-related sources and toward VCPs. Existing U.S. regulations on VCPs emphasize mitigating ozone and air toxics, but they currently exempt many chemicals that lead to secondary organic aerosols.
Atomic-resolution transmission electron microscopy of electron beam–sensitive crystalline materials

Daliang Zhang, Yihan Zhu, Lingmei Liu, Xiangrong Ying, Chia-En Hsiung, Rachid Sougrat, Kun Li, Yu Han

Science 2017, (359) 6376, 675.

Abstract

High-resolution transmission electron microscopy is an invaluable tool for looking at the crystalline structures of many materials. However, the need for high beam doses, especially as a sample is rotated to find the crystal axes, can lead to damage, particularly in fragile materials. Zhang et al. combined a state-of-the-art direct-detection electron-counting camera with ways to limit the overall electron dose to analyze delicate materials such as metal organic frameworks. With this approach, they could see the benzene rings in a UiO-66 linker and the coexistence of ligand-free (metal-exposing) and ligand-capped surfaces in UiO-66 crystals.
Abstract

The kinetics and diastereoselectivity of the Mukaiyama aldol reaction between C,O,O-Tris(trimethylsilyl)ketene acetal and aldehydes bearing alkyl, vinyl, and aromatic substituents is influenced by the nature of Lewis acid catalysts. A density functional theory investigation using the M06-2X exchange-correlation functional and the PCM scheme to account for solvent effects has been carried out to characterize the structure and energetics of the transition state when the Lewis acid is ZnBr$_2$ (MX$_2$) or GaCl$_3$ (MX$_3$) in comparison to the uncatalyzed reaction. The main observations are that (i) the pro-syn transition states are always more stable than the pro-anti ones; (ii) for MX$_2$, the transition state presents a cyclic structure, whereas it is open for MX$_3$, owing to steric interactions; (iii) the difference of activation free enthalpy between the pro-anti and pro-syn transition states decreases when the reaction is catalyzed, by either MX$_2$ or MX$_3$, demonstrating a reduction of the diastereoselectivity with respect to the uncatalyzed reaction; (iv) this decrease of diastereoselectivity is larger for MX$_3$ than for MX$_2$-catalyzed reactions; and (v) the MX$_3$-catalyzed reactions are kinetically favored by 1–2 kcal mol$^{-1}$ with respect to the MX$_2$ ones.
Monitoring the Interaction of CO with Graphene Supported Ir Clusters by Vibrational Spectroscopy and Density Functional Theory Calculations

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Abstract

The interaction of carbon monoxide (CO) with graphene supported Ir cluster (Ir/graphene/Ir(111)) and a Ir(111) single crystal surface was studied by infrared reflection–adsorption spectroscopy (IRRAS). The cluster morphology was characterized by scanning tunneling microscopy and density functional theory (DFT) calculations predicted the adsorption frequencies of CO molecules on the Ir single crystal surface and clusters. After exposing the clean Ir(111) surface to CO at 195 K, one intense vibrational band is observed at 2043 cm$^{-1}$, which is assigned to on top CO species. This band shifts to a much higher frequency at 2082 cm$^{-1}$ at higher CO exposure. After exposing clean graphene/Ir(111) to CO at 195 K, no CO band was observed in the IR spectra, which confirms a full graphene layer over the Ir(111) surface. However, CO molecules adsorb on Ir clusters supported on graphene/Ir(111) at 195 K. For the 0.05, 0.1, 0.15, and 0.2 ML Ir clusters, two IR bands were observed at 2060 and 2088 cm$^{-1}$, 2050 and 2070 cm$^{-1}$, 2048 and 2070 cm$^{-1}$, and 2052 and 2070 cm$^{-1}$, respectively. The IR bands at lower frequencies are assigned to the CO on one-layer high clusters, and the IR bands at higher frequencies are assigned to the CO adsorption on two- or several-layer high clusters. The IR frequencies of CO adsorbed on clusters are shifted to lower wavenumbers compared to those observed on the single crystal surface, which is in agreement with DFT calculations. The IRRAS data recorded after CO adsorption on Ir clusters at different temperatures demonstrate that CO species are stable up to 350 K, although the intensity of CO on top one-layer high cluster reduces largely, indicating CO-induced cluster sintering.