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**Epoxidized vegetable oil and bio-based materials as PVC plasticizer**

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- By Hosney, Hadeel; Nadiem, Bassant; Ashour, Ibrahim; Mustafa, Ibrahim; El-Shibiny, Ayman
- From Journal of Applied Polymer Science (2018), 135(20), n/a. | Language: English, Database: CAPLUS

- A review. Phthalate esters received a considerable attention owing to its various applications and the harmful health effects resulting from phthalate exposure; thus, finding an alternative to phthalate derivs. became a necessity. Phthalate esters are commonly used as plasticizer in polymer formulation; in particular for poly(vinyl chloride) (PVC) formulation. According to the researches in the last 18 years, epoxidized vegetable oils are one of the alternatives that are strongly encouraged to substitute phthalate esters since they were proven to be valid in various applications, eco-friendly and sustainable resource. However, most of the prodn. practices for epoxidized vegetable oil are via conventional epoxidn. that concs. on a catalyst that is homogeneous and non-reusable. This type of catalyst, however, causes several problems later in the process. Therefore, the selective epoxidn. of vegetable oils process requires new catalytic systems that are more aligned with the green chem. principles. This article reviews the harmful health effects assocd. with the exposure to phthalate esters products, explains the usage of oleochem. resources as a substitute to phthalate esters and describes different approaches for the epoxidn. of vegetable oils. Finally, it draws attention to the usage of epoxy and bio-based compds. as plasticizers in PVC manufg. © 2018 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2018, 135, 46270.

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**The Methanol Economy: Methane and Carbon Dioxide Conversion**

- By Liu, Wen-Chi; Baek, Jayeon; Somorjai, Gabor A.
- From Topics in Catalysis (2018), 61(7-8), 530-541. | Language: English, Database: CAPLUS

- A review. Need for clean energy is imminent and methanol is considered as a promising alternative energy source. Conventional process for the prodn. of methanol has been achieved via syngas which is derived by the steam reforming of methane or naphtha and the gasification of coal. Methanol can also be prepd. by direct oxidn. of methane (natural gas) or redn. of carbon dioxide (CO2) with hydrogen. In this way, carbon-neutral cycling can be achieved and world's dependence on fossil fuels will be alleviated. In this minireview, we will address case by case some recent advancements in the conversion of methane and CO2 to methanol both homogeneously and heterogeneously with emphasis on the contribution from Professor George A. Olah's and our group. In the end, a short outlook is provided towards existing problems and future opportunities.

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**Homogeneous Catalytic Reduction of CO2 with Silicon-Hydrides, State of the Art**

- By Fernandez-Alvarez, Francisco J.; Oro, Luis A.

- A review. During recent years, the catalytic transformation of CO, using silicon-hydrides as reductants has emerged as a promising methodol. that allows the selective redn. of CO, to the formate, formaldehyde, methoxide or methane level under mild reaction conditions. Moreover, some catalysts have been employed for the formylation and/or methylation of the N-H bonds of secondary and/or primary amines by their reaction with CO, and hydrosilanes. This work summarizes the different catalytic systems that have shown to be efficient for the above-mentioned reactions. Furthermore, a brief description of the reactions performance and the conditions employed in each case is included.
**Pinenes: Abundant and Renewable Building Blocks for a Variety of Sustainable Polymers**

- By Winnacker Malte
- From Angewandte Chemie (International ed. in English) (2018). | Language: English, Database: MEDLINE

Pinenes - a group of monoterpenes containing a double bond - are very suitable renewable building blocks for a variety of **sustainable polymers** and materials. Their abundance from mainly non-edible parts of plants as well as the feasibility to isolate them render these compounds unique amongst the variety of biomass that is utilizable for novel materials. Accordingly, their use for the synthesis of biobased **polymers** has been investigated intensively, and strong progress has been made with this especially within the past 2-3 years. Direct cationic or radical polymerization via the double bonds as well as polymerization upon their further functionalization can afford a variety of **sustainable polymers** suitable for many applications, which is summarized in this article.

**Selective production of linear α-olefins via catalytic deoxygenation of fatty acids and derivatives**

- By Chatterjee, Anamitra; Hopen Eliasson, Sondre H.; Jensen, Vidar R.
- From Catalysis Science & Technology (2018), 8(6), 1487-1499. | Language: English, Database: CAPLUS

A review. Scientists are exploring renewables as sources for a more sustainable prodn. of chems. Linear α-olefins (LAOs) are key commodity chems. and petrochem. intermediates, which are currently almost exclusively obtained from fossil resources. The most important renewable alternative is plant oil, from which fatty acids and their derivs. can be converted into LAOs by ethenolysis of monounsaturated fatty acids or deoxygenation of saturated ones. The variety, in terms of length, is greater for the saturated fatty acids found in plant oils, and this review covers deoxygenation processes mediated by homogeneous, heterogeneous and enzymic catalysts and discusses the strengths and weaknesses of different approaches for the selective prodn. of LAOs. Although progress has been made in recent years, the best catalysts in each category are still far from fulfilling the industrial requirements for efficiency, atom economy, and turnover nos. We hope that our focus on the main remaining challenges will stimulate future research to develop catalyzed deoxygenation of fatty acid derivs. as a sustainable and industrially viable route to a range of α-olefins.

**Homogeneous Catalysis for Sustainable Hydrogen Storage in Formic Acid and Alcohols**

- By Sordakis, Katerina; Tang, Conghui; Vogt, Lydia K.; Junge, Henrik; Dyson, Paul J.; Beller, Matthias; Laurenzcy, Gabor

A review. Hydrogen gas is a storable form of chem. energy that could complement intermittent renewable energy conversion. One of the main disadvantages of hydrogen gas arises from its low d., and therefore, efficient handling and storage methods are key factors that need to be addressed to realize a hydrogen-based economy. Storage systems based on liqs., in particular, formic acid and alcs., are highly attractive hydrogen carriers as they can be made from CO₂ or other renewable materials, they can be used in stationary power storage units such as hydrogen filling stations, and they can be used directly as transportation fuels. However, to bring about a paradigm change in the energy infrastructure, efficient catalytic processes that release the hydrogen from these mols., as well as catalysts that regenerate these mols. from CO₂ and hydrogen, are required. In this review, the considerable progress is described that has been made in homogeneous catalysis for these crit. reactions, namely, the hydrogenation of CO₂ to formic
acid and methanol and the reverse dehydrogenation reactions. The dehydrogenation of higher alcohols available from renewable feedstocks is also described. Key structural features of the catalysts are analyzed, as is the role of additives, which are required in many systems. Particular attention is paid to advances in sustainable catalytic processes, esp. to additive-free processes and catalysts based on Earth-abundant metal ions. Mechanistic information is also presented, and it is hoped that this review not only provides an account of the state of the art in the field but also offers insights into how superior catalytic systems can be obtained in the future.

Homogeneous Oxygenase Catalysis

By Liang, Yujie; Wei, Jialiang; Qiu, Xu; Jiao, Ning
From Chemical Reviews (Washington, DC, United States) (2018), 118(10), 4912-4945. | Language: English, Database: CAPLUS

A review. Oxygenases-catalyzed reductive activation of molecular oxygen and incorporation of O atoms into an organic mol. is undoubtedly one of the most attractive research areas. Typically, these oxygenation reactions proceed with high selectivity and reactivity, which is seldom found in its "biomimetic" chemocatalytic counterparts. Furthermore, enzymic oxygenation can avoid undesired overoxidation, which is frequently observed in (industrial) chemical transformation. Therefore, it is not surprising that tremendous attention has been paid to enzymic oxygenation. Their application in organic synthesis has been steadily growing over the years. The goal of the present Review is to provide a handy ref. for chemists interested in using homogeneous oxygenase catalysis and those interested in discovering new types of biomimetic oxidations and oxygenations with dioxygen. In this Review, we will review the recent advances in homogeneous oxygenase catalysis to reveal the great achievements and potentials in this field.

Oxygen Reduction by Homogeneous Molecular Catalysts and Electrocatalysts

By Pegis, Michael L.; Wise, Catherine F.; Martin, Daniel J.; Mayer, James M.

A review of sol. mol. catalysts and electrocatalysts for the ORR. The O reduction reaction (ORR) is a key component of biological processes and energy technologies. The precise synthetic control and relative ease of mechanistic study for homogeneous mol. catalysts, as compared to heterogeneous materials or surface-adsorbed species, enables a detailed understanding of the individual steps of ORR catalysis. Thus, the Review places particular emphasis on ORR mechanism and thermodynamics. First, the thermochem. of O reduction and the factors influencing ORR efficiency are described to contextualize the discussion of catalytic studies that follows. Reports of ORR catalysis are presented in terms of their mechanism, with sep. sections for catalysis proceeding via initial outer- and inner-sphere electron transfer to O. The rates and selectivities (for prodn. of H₂O₂ vs. H₂O) of these catalysts are provided, along with suggested methods for accurately comparing catalysts of different metals and ligand scaffolds that were examined under different exptl. conditions.
A review. The authors consider the use of mol. oxygen in reactions mediated by polyoxometalates. Polyoxometalates are anionic metal oxide clusters of a variety of structures that are sol. in liq. phases and therefore amenable to homogeneous catalytic transformations. Often, they are active for electron transfer oxidns. of a myriad of substrates and upon redn. can be reoxidized by mol. oxygen. For example, the phosphovanadomolybdate, \( \text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40} \), can oxidize Pd(0) thereby enabling aerobic reactions catalyzed by Pd and \( \text{H.PV.Mo}_{10}\text{O}_{40} \). In a similar vein, polyoxometalates can stabilize metal nanoparticles, leading to addnl. transformations. Furthermore, electron transfer oxidn. of other substrates such as halides and sulfur-contg. compds. is possible. More uniquely, \( \text{H.PV.Mo}_{10}\text{O}_{40} \) and its analogs can mediate electron transfer-oxygen transfer reactions where oxygen atoms are transferred from the polyoxometalate to the substrate. This unique property has enabled correspondingly unique transformations involving carbon-carbon, carbon-hydrogen, and carbon-metal bond activation. The pathway for the reoxidn. of vanadomolybdates with \( \text{O}_2 \) appears to be an inner-sphere reaction, but the oxidn. of one-electron reduced polyoxotungstates has been shown through intensive research to be an outer-sphere reaction. Beyond electron transfer and electron transfer-oxygen transfer aerobic transformations, there a few examples of apparent dioxygenase activity where both oxygen atoms are donated to a substrate.

A review. In this Perspective, we outline recent examples of homogeneous transition-metal hydrogen transfer catalysts for which functionality within the complex's outer coordination sphere influences the outcome of a reaction. Secondary-sphere groups are often applied to hydrogen transfer reactions, but their specific role during catalysis is not always well-understood. New expl. and theor. work details the complexity assocd. with predicting secondary-sphere interactions and therefore designing improved catalysts. This Perspective highlights examples of catalysts contg. secondary-sphere groups that (1) accelerate a key turnover-limiting step such as \( \text{H}_2 \) heterolysis or hydride transfer, (2) limit competing catalytic cycles, (3) prevent catalyst decompn., and/or (4) provide access to new catalysts through postmetatation modifications. The examples described herein emphasize numerous roles of the secondary sphere in hydrogen transfer catalysis and illustrate how the optimal use of these interactions is predicated on the analyses of key reaction intermediates in a catalytic reaction.
Iridium-based hydride transfer catalysts: from hydrogen storage to fine chemicals

By Lu, Zhiyao; Cherepakhin, Valeriy; Demianets, Ivan; Lauridsen, Paul J.; Williams, Travis J.
From Chemical Communications (Cambridge, United Kingdom) (2018), 54(56), 7711-7724. | Language: English, Database: CAPLUS

Selective hydrogen transfer remains a central research focus in catalysis: hydrogenation and dehydrogenation have central roles, both historical and contemporary, in all aspects of fuel, agricultural, pharmaceutical, and fine chem. synthesis. Our lab has been involved in this area by designing homogeneous catalysts for dehydrogenation and hydrogen transfer that fill needs ranging from on-demand hydrogen storage to fine chem. synthesis. A keen eye toward mechanism has enabled us to develop systems with excellent selectivity and longevity and demonstrate these in a diversity of high-value applications. Here we describe recent work from our lab in these areas that are linked by a central mechanistic trichotomy of catalyst initiation pathways that lead highly analogous precursors to a diversity of useful applications.

Manganese Complexes for (De)Hydrogenation Catalysis: A Comparison to Cobalt and Iron Catalysts

By Kallmeier, Fabian; Kempe, Rhett

A review. The sustainable use of the resources on our planet is essential. Noble metals are very rare and are diversely used in key technologies, such as catalysis. Manganese is the third most abundant transition metal of the Earth’s crust and based on the recently discovered impressive reactivity in hydrogenation and dehydrogenation reactions, is a potentially useful noble-metal “replacement”. The hope of novel selectivity profiles, not possible with noble metals, is also an aim of such a "replacement". The reactivity of manganese complexes in (de)hydrogenation reactions was demonstrated for the first time in 2016. Herein, we summarize the work that has been published since then and esp. discuss the importance of homogeneous manganese catalysts in comparison to cobalt and iron catalysts.

The Direct Catalytic Oxidation of Methane to Methanol-A Critical Assessment

By Ravi, Manoj; Ranocchiari, Marco; van Bokhoven, Jeroen A.

Despite the large no. of disparate approaches for the direct selective partial oxidn. of methane, none of them has translated into an industrial process. The oxidn. of methane to methanol is a difficult, but intriguing and rewarding, task as it has the potential to eliminate the prevalent natural gas flaring by providing novel routes to its valorization. This Review considers the synthesis of methanol and methanol derivs. from methane by homogeneous and heterogeneous pathways. By establishing the severe limitations related to the direct catalytic synthesis of methanol from methane, we highlight the vastly superior performance of systems which produce methanol derivs. or incorporate specific measures, such as the use of multicomponent catalysts to stabilize methanol. We thereby identify methanol protection as being indispensable for future research on homogeneous and heterogeneous catalysis.
Recent Developments in the Scope, Practicality, and Mechanistic Understanding of Enantioselective Hydroformylation

By Brezny Anna C; Landis Clark R

From Accounts of chemical research (2018). | Language: English, Database: MEDLINE

In the nearly 80 years since catalytic hydroformylation was first reported, hundreds of billions of pounds of aldehyde have been produced by this atom efficient one-carbon homologation of alkenes in the presence of H2 and CO. Despite the economy and demonstrated scalability of hydroformylation, the enantioselective process (asymmetric hydroformylation, AHF) currently does not contribute significantly to the production of chiral aldehydes and their derivatives. Current impediments to practical application of AHF include low diversity of chiral ligands that provide effective rates and selectivities, limited exploration of substrate scope, few demonstrations of efficient flow reactor processes, and incomplete mechanistic understanding of the factors that control reaction selectivity and rate. This Account summarizes developments in ligand design, substrate scope, reactor technology, and mechanistic understanding that advance AHF toward practical and atom-efficient production of chiral α-stereogenic aldehydes. Initial applications of AHF were limited to activated terminal alkenes such as styrene, but recent developments enable high selectivity for unactivated olefins and more complex substrates such as 1,1'- and 1,2-disubstituted alkenes. Expanded substrate scope primarily results from new chiral phosphine ligands, especially phospholanes and bisdiazaphospholanes (BDPs). These ligands are now more accessible due to improved synthesis and resolution procedures. One of the virtues of diazaphospholanes is the relative ease of derivatization, including attachment to heterogeneous supports. Hydroformylation involves toxic and flammable reactants, a serious concern in pharmaceutical production facilities. Flow reactors offer many process benefits for handling dangerous reagents and for systematically moving from research to production scales. New approaches to achieving good gas-liquid mixing in flow reactors have been demonstrated with BDP-derived catalyst systems and lend assurance that AHF can be practically implemented by the pharmaceutical and fine chemical industries. To date, progress in AHF has been empirically driven, because hydroformylation is a complex, multistep process for which the origins of chemo-, regio-, and enantioselectivity are difficult to elucidate. Mechanistic complexity arises from three concurrent catalytic cycles (linear and two diastereomeric branched paths), significant pooling of catalyst as off-cycle species, and multiple elementary steps that are kinetically competitive. Addressing such complexity requires new approaches to collecting kinetic and extra-kinetic information and analyzing these data. In this Account, we describe our group's progress toward understanding the complex kinetics and mechanism of AHF as catalyzed by rhodium bis(diazaphospholane) catalysts. Our strategy features both "outside-in" (i.e., monitoring catalytic rates and selectivities as a function of reactant concentration and temperature) and "inside-out" (i.e., building kinetic models based on the rates of component steps of the catalytic reaction) approaches. These studies include isotopic labeling, interception and characterization of catalytic intermediates using NMR techniques, multinuclear high-pressure NMR spectroscopy, and sophisticated kinetic modeling. Such broad-based approaches illuminate the kinetic and mechanistic origins of selectivity and activity of AHF and the elucidation of important principles that apply to all catalytic reactions.

Recent advances in ruthenium-based olefin metathesis

By Ogba, O. M.; Warner, N. C.; O'Leary, D. J.; Grubbs, R. H.

From Chemical Society Reviews (2018), 47(12), 4510-4544. | Language: English, Database: CAPLUS

Ruthenium-based olefin metathesis catalysts, known for their functional group tolerance and broad applicability in org. synth. technol. in these areas. A discussion of recent mechanistic investigations is followed by an overview of selected applications...
Low-valent group 14 element hydride chemistry: towards catalysis

By Hadlington, Terrance J.; Driess, Matthias; Jones, Cameron
From Chemical Society Reviews (2018), 47(11), 4176-4197. | Language: English, Database: CAPLUS

The chem. of group 14 element(II) hydride complexes has rapidly expanded since the first stable example of such a compd. was reported in 2000. Since that time it has become apparent that these systems display remarkable reactivity patterns, in some cases mimicking those of late transition-metal (TM) hydride compds. This is esp. so for the hydroelementation of unsatd. org. substrates. Recently, this aspect of their reactivity has been extended to the use of group 14 element(II) hydrides as efficient, "TM-like" catalysts in org. synthesis. This review will detail how the chem. of these hydride compds. has advanced since their early development. Throughout, there is a focus on the importance of ligand effects in these systems, and how ligand design can greatly modify a coordinated complex’s electronic structure, reactivity, and catalytic efficiency.

Iron-catalyzed dehydrogenation reactions and their applications in sustainable energy and catalysis

By Balaraman, Ekambaram; Nandakumar, Avanashiappan; Jaiswal, Garima; Sahoo, Manoj K.
From Catalysis Science & Technology (2017), 7(15), 3177-3195. | Language: English, Database: CAPLUS

A review. Inspired by nature, chemists have designed new catalysts in the pursuit of selective bond activation and chem. transformations. Emergent biol. systems often use earth-abundant first-row transition elements as catalytically active sites to facilitate specific and highly selective chem. processes. The design of a new catalytic system based on abundant and inexpensive catalysts, particularly the iron-based catalysts, for fundamentally significant synthetic transformations under environmentally benign conditions is an important paradigm in chem. synthesis. In recent times, iron-based catalytic systems have shown unprecedented reactivity in the acceptorless dehydrogenation reactions of feedstock chems., with the liberation of mol. hydrogen as the byproduct, and have enabled greener chem. synthetic methods and alternative energy storage systems. Indeed, it has been demonstrated that the proper design of iron catalysts by judiciously choosing ligands, can aid in the development of new sustainable energy storage systems and catalysis. This tutorial review focuses on the recent development of iron-based dehydrogenation reactions of fundamentally important feedstock, as a route to sustainable chem. synthesis and energy storage applications. The emerging area of the iron-based dehydrogenation strategy provides an opportunity to make industrially applicable, cost-effective and environmentally benign catalytic systems.

Supramolecular Approaches To Control Activity and Selectivity in Hydroformylation Catalysis

By Nurttila, Sandra S.; Linnebank, Pim R.; Krachko, Tetiana; Reek, Joost N. H.

A review. The hydroformylation reaction is one of the most intensively explored reactions in the field of homogeneous transition metal catalysis, and many industrial applications are known. However, this atom economical reaction has not been used to its full potential, as many selectivity issues have not been solved. Traditionally, the selectivity is controlled by the ligand that is coordinated to the active metal center. Recently, supramol. strategies have been demonstrated to provide powerful complementary tools to control activity and selectivity in hydroformylation reactions. In this review, we will highlight these supramol. strategies. We have organized this paper in sections in which we describe the use of supramol.
bidentate ligands, substrate preorganization by interactions between the substrate and functional groups of the ligands, and hydroformylation catalysis in mol. cages.

**Advances in One-Pot Synthesis through Borrowing Hydrogen Catalysis**

A review. The **borrowing** H (BH) principle, also called H autotransfer, is a powerful approach which combines transfer hydrogenation (avoiding the direct use of mol. H) with one or more intermediate reactions to synthesize more complex mols. without the need for tedious sepn. or isolation processes. The strategy which usually relies on three steps, (i) dehydrogenation, (ii) intermediate reaction, and (iii) hydrogenation is an excellent and well-recognized process from the synthetic, economic, and environmental point of view. In this context, the objective of the present review is to give a global overview on the topic starting from those contributions published prior to the emergence of the BH concept to the most recent and current research under the term of BH catalysis. Two main subareas of the topic (homogeneous and heterogeneous catalysis) were identified, from which three subheadings based on the source of the electrophile (alkanes, alcs., and amines) were considered. Then the type of bond being formed (C-C and C-heteroatom) was taken into account to end-up with the intermediate reaction working in tandem with the metal-catalyzed hydrogenation/dehydrogenation step. The review was completed with the more recent advances in asym. catalysis using the BH strategy.

**Cobalt Complexes as an Emerging Class of Catalysts for Homogeneous Hydrogenations**

Catalytic hydrogenation using mol. hydrogen represents a green and practical approach for redns. of all kinds of org. chems. Traditionally, in the majority of these processes the presence of transition metal catalysts is required. In this regard, noble-metal-based catalysts have largely been implemented, such as the application of iridium, palladium, rhodium, ruthenium, and others. Recently, the employment of earth-abundant 3d metals has emerged to replace the utilization of scarce noble metals because of their availability, lower cost, and often reduced toxicity. In this respect, several cobalt complexes, in the form of either molecularly well-defined or in situ-formed complexes, are receiving increasing attention from the scientific community. Importantly, the stability and reactivity of the complexes have greatly been supported by multidentate ligands under steric and/or electronic influences. For instance, tridentate or tetradentate phosphine ligands indirectly tune the reactivity of the metal center to accelerate the overall process, whereas direct participation of the ligand in pincer-type complexes through ligand-metal cooperation regulates the elementary steps in the catalytic cycle. In this Account, we emphasize specifically the advancements in cobalt-catalyzed hydrogenations using mol. hydrogen accomplished in our group. A variety of substrate classes ranging from simple mols. (e.g., carbon dioxide) to complex compds. were
explored under the mild and efficient catalytic conditions. Notable examples include the redn. of carbon dioxide to afford either formates using a Co(BF₄)·6H₂O/Tetraphos catalyst system or methanol employing a Co(acac)/Triphos complex in the presence of HNTf₂. As interesting examples of the synthesis of fine chems., cobalt-promoted hydrogenations of nitriles to primary amines and reductive alkylations of indoles using carboxylic acids as alkylating agents are highlighted. Moreover, highly selective hydrogenations of N-heteroarenes under additive-free conditions were possible by the application of specific cobalt complexes. More recently, a set of carboxylic esters could be hydrogenated to the corresponding alics. with high efficiency by the use of a well-defined cobalt-PNP pincer catalyst. In particular, the decent reactivity of cobalt catalysts enabled high selectivity and functional group tolerance to be achieved. Throughout our studies, it was found that the pairing of a suitable cobalt precursor and an appropriate tridentate or tetradeutate phosphine ligand plays a crucial role harnessing the desired reactivity, while other monodentate and bidentate phosphine ligands showed no reactivity in these investigations. Our developments could provide supervisory information for the future exploration of cobalt-catalyzed hydrogenation reactions and other types of reactions involving cobalt catalysis. Furthermore, relevant contributions from other groups, remaining challenges, and future perspectives in this research area are also presented.