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The Christmas Tree

Transformation of
Abies Grandis
into
Renewable Fuels
and Chemicals

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Transformation of *Abies Grandis* into Renewable Fuels and Chemicals

Atef S. Iskander

Biomass utilization has received much attention due to growing environmental concern about climate change and the depletion of oil reserves. The selection of biofuel candidates and promising technologies to produce them is a great challenge. In order to tackle such challenge, two key aspects must be taken into consideration: the ability to utilize a range of feedstocks and the application of carbon efficient processes to produce fuels. Terpenes are versatile and sustainable platform components that can be produced from a variety of forestry residues. Herein. a proposal presents the advantage of utility of one of Christmas trees family, *Abies grandis* (*grand fir*) as an energy source and how to produce high-density renewable fuels and a range of commodity chemicals from this sustainable source, which will pave the way to enhance the reduction in greenhouse gas emissions.

Keywords: Terpenes; Abies grandis; renewable fuels; heterogeneous catalysis; biorefinery

1. *Introduction*

Growing environmental concern about climate change and diminishing petroleum resources have made the search for renewable resource options a quite challenge. Such renewable energy resources are derived from sources that can be naturally replenished such as solar, wind, mini hydro, geothermal and energy produced from biomass. Plant biomass utilization is one of the most important resources for biofuel production. In addition, it can also be the reservoirs of chemicals, pharmaceuticals and food additives. The biofuel has to satisfy so many criteria. It should be cheap. It should have a high energy to mass ratio; it should be highly combustible. It should be stable upon long-term storage. It should have the right physical properties; a liquid; and it should be transportable by pipeline. In an ideal world we want our biofuel to be relative to conventional fossil fuel, but at the same time we want our fuel to be as such its combustion does not increase current net atmospheric levels of CO_2. Given all these and many other demands, it is likely that so many types of energy sources will come to predominate over fossil fuels and delivering actual and sustainable reductions in greenhouse gases (GHG) emissions.

A major biological raw material for making fuels is the plant cell wall. Microbes annually hydrolyze 10^{11} tons of plant biomass, principally plant cell wall material, that contains the energetic equivalent of 640 billion barrels of crude oil.[1] Arguably, effective biomass utilization will require more widespread use of its biological material. For instance, complex energy feedstocks such as forestry residues represent a vastly underutilized renewable power source. These materials can be harnessed to produce a variety of products, from fuels to commodity chemicals, while drastically reducing net carbon emissions and providing for a sustainable future. In this context, I offer a proposal that presents the advantage of utility of one of Christmas trees family, *Abies grandis* (*grand fir*) as an energy source and how to produce high-density renewable fuels and a range of commodity chemicals from this sustainable source. The emergence of new technologies for the production of biofuels and chemicals from a large amounts of monoterpene content of *Abies Grandis* will pave the way to enhance the reduction in greenhouse gas emissions.

2. Proposed Technical Approach

2.1 Abies Grandis as a renewable and sustainable source of biofuel production

If we made a general survey on the energy content of the different biomass products, terpenes would be top on the list, followed by vegetable oils, lignin, and sugars. Terpenes such as α-pinene, β-pinene, camphene, and limonene are components of pine resin, and produced industrially either by tapping trees (gum turpentine) or as byproducts of paper pulping. However, if terpenes can be used for biofuel, then *Abies grandis* can be employed for this purpose due to its high amounts of monoterpene content. Besides, it can be used for synthesizing products with a higher added value, such as chemicals and fine chemicals.

2.2 Abies Grandis advantages

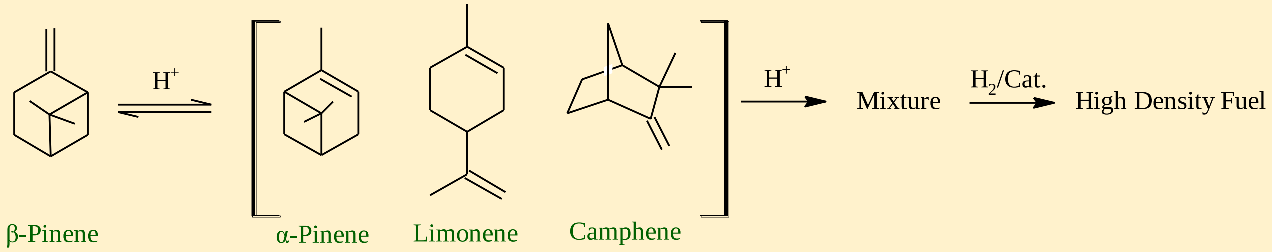
Attractive features of using *Abies Grandis* as fuels production are:

i) It is a fast growing coniferous tree with a high potential for sustainable wood production. At maturity, the typical Grand Fir (Abies Grandis) will reach up to 200 feet high, with a maximum height at 20 years of 25 feet.
ii) Domestically, it grows in some forest regions in Europe and the Pacific Northwest including British Columbia, Alberta, Washington State, Oregon, Idaho and the west of Montana.

iii) It has a large amounts of monoterpene content.
iv) It is biodegradable.
v) It is a carbon-neutral resource that burns more cleanly than fossil fuels.
vi) It can generate the best fuel molecule(s) that relative to conventional fuel.
vii) It has the potential to produce a wide range of chemicals that have applications in many industries.

2.3 Terpenes as source of fuels and chemicals

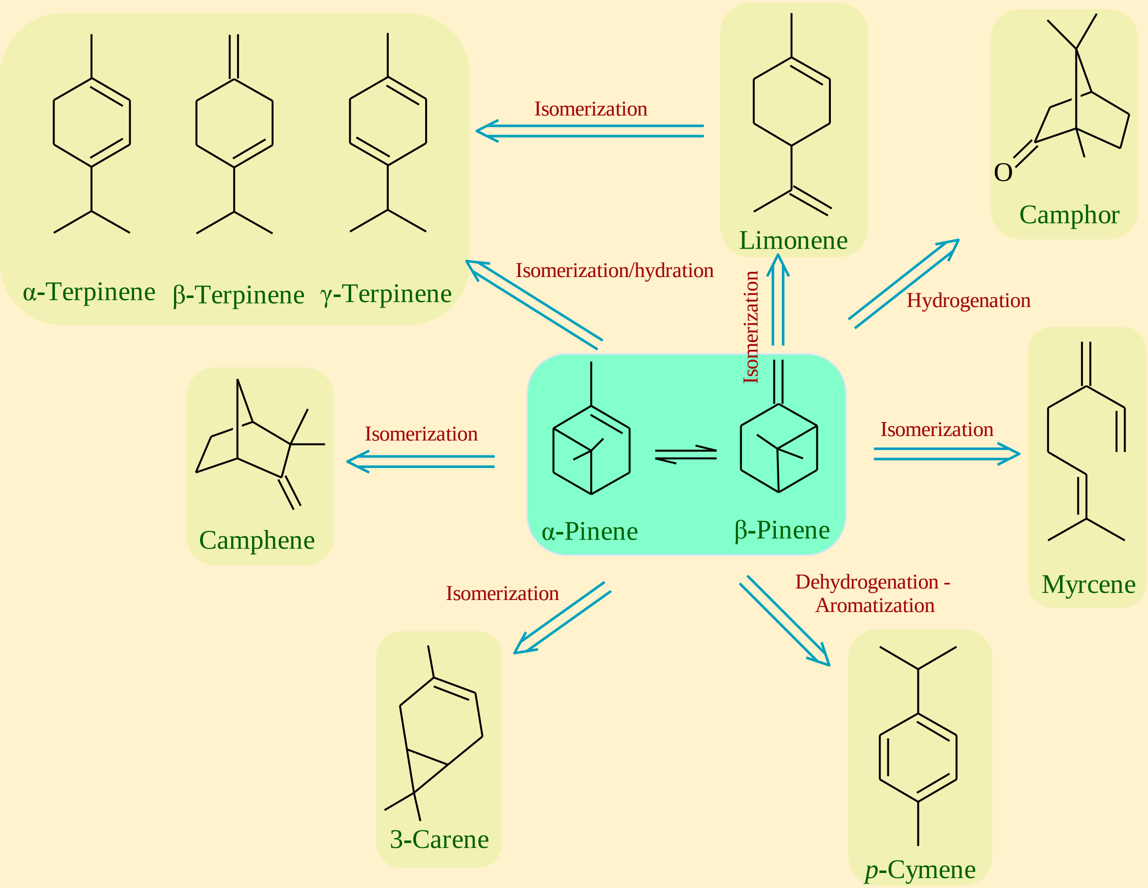
Terpenes are hydrocarbons that contain one or more double bonds. The most important sources of terpenes are the turpentine oleoresins extracted from coniferous trees; terebinth. The turpentine fraction of the oleoresins is a complex mixture of monoterpene (C_{10}) olefins in which limonene, *α*-pinene, and *β*-pinene are prominent components. Turpentine was used as renewable fuels as far back as the early 19th century. It has an exceptional volumetric net heat of combustion and low volatility. Since the production of turpentine is too low to meet the requirements for biofuels, there are abundant and inexpensive natural components, such as limonene, camphene or pinene, that represent a sustainable and versatile feedstock for fuels and chemicals. For instance, a series of high density renewable fuels has been synthesized through selective dimerization of pure as well as mixtures of α-pinene, camphene, limonene, and crude turpentine using the heterogeneous catalysts Nafion, Nafion SAC-13, and Montmorillonite K-10 (Scheme 1).[2] They have the potential use as significant components of jet, diesel and tactical fuels.



Scheme 1. Isomerization/dimerization of *β*-pinene.

Transferring biomass-derived cyclic ketones such as cyclopentanone and cyclohexanone to a mono-condensed product through aldol self-condensation has been achieved for high-density biofuels production. The encapsulation of phosphotungstic acid clusters within the cages of a MIL-101 MOF enhances selectivity the process.[3]

A large number of chemicals can be prepared from terpenes. For example, the *α*- and *β*-pinenes constitute real building blocks for the synthesis of a wide range of chemicals for use as fragrances, flavors, pharmaceuticals, solvents, etc.[4] Scheme 2 shows some valuable compounds that can be obtained from pinene.



Scheme 2. Some valuable transformations of pinene.

2.4 New Fuels derived from A. grandis

The natural advantages of these hydrocarbons can be obtained from *A. Grandis* that contains up to 60% of pinene beside other important components. Therefore, the development of methods to both produce and utilize terpenes as fuels, on a relevant scale, is quite compelling.

The development of saturated hydrocarbon fuels based on *A. Grandis* feedstocks may lie in strong heterogeneous acids to produce complex molecules whether through dimerization of pure component or polymerization of mixtures of different components. Heterogeneously catalyzed conversions that employs transition metal nanoparticles, are particularly attractive due to their superior chemical and thermal tolerance, lower cost, safer storage and handling, and amenability to continuous processing compared with enzymatic or homogeneous analogues. Figure 1 presents a schematic illustration of the proposed biorefinery.

3. Conclusion

Concerns linked to climate change and depletion of oil reserves are providing the necessary impetus for new energy source that will use biomass as its primary source of carbon and energy. In this regard, the proposed approach will allow the conversion of terpenes derived from *Abies grandis* to produce fuels. *Abies grandis* is a fast growing coniferous tree with a high potential for sustainable wood production that can be used as biomass feedstock. This plant biomass features high amounts of monoterpene content. The proposal highlights the possibility of dimerization/polymerization of extracted components to produce high-density renewable fuels and a range of commodity chemicals as well as the need to develop strong heterogeneous catalysts. The ultimate goal of this proposal is to supply high performance renewable fuels as well as a range of products for a series of very different markets.

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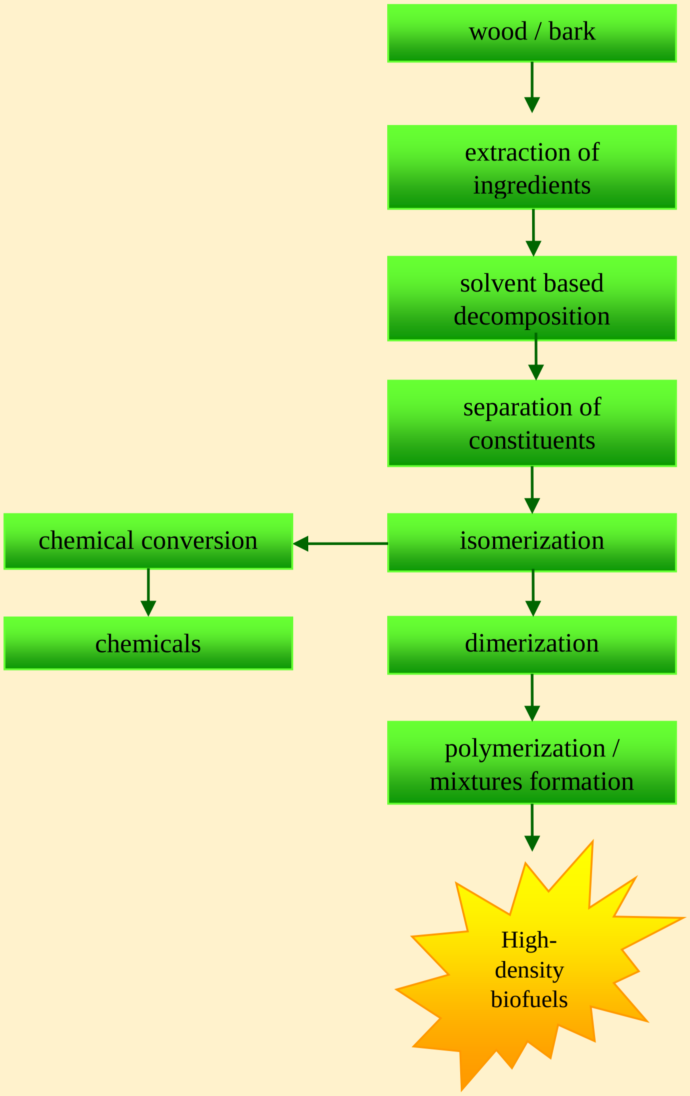

Figure 1. A schematic illustration for transformation of *Abies Grandis* into renewable fuels and chemicals

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Snapshots of some topics of interest of recent notable advances in chemistry

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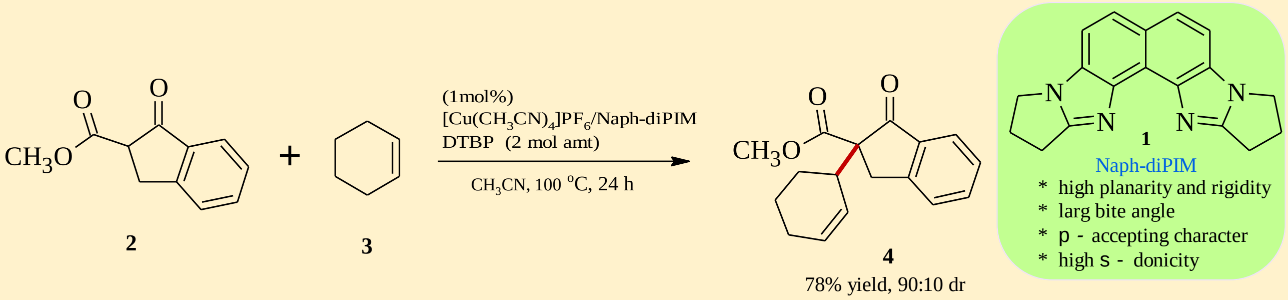
Managing Director / Founder

Bisamidine-Cu(I)-mediated C-Allylation of 1,3-Dicarbonyl Compounds with Simple Cyclic Alkenes Using Di-*tert*-butyl Peroxide

A Cu(I) complex of bisamidine-type sp^{2}N bidentate ligand, Naph-diPIM, catalyzes sp^{3}CH/sp^{3}CH dehydrogenative coupling between 1,3-dicarbonyl compounds and simple cyclic alkenes using di-*tert*-butyl peroxide (t-BuO)$_2$.

A new molecular catalyst composed of a cationic Cu(I) complex, [Cu(CH$_3$CN)$_4$]PF$_6$, and bisamidine ligand Naph-diPIM **1**, 1,2,11,12-tetrahydronaphtho[1,2-*b*:7,7-*b′*]dipyrrolo-imidazole, induced the coupling between 1,3-dicarbonyl compounds, 2-(methoxycarbonyl)indan-1-one **2**, and simple cyclic alkenes, cyclohexene **3,** in the presence of (t-BuO)$_2$ (DTBP) to afford the corresponding C-allylation products with up to > 99:1 diastereomer ratio with easily removable *t*-BuOH coproduct (Scheme 1).



Scheme 1 Oxidative coupling of 2-(methoxycarbonyl)indan-1-one **2** and cyclohexene **3** with DTBP catalyzed by Naph-diPIM **1**-metal Cu(I)-complex.

Furthermore, the oxidative C-H allylation was extended to the asymmetric version using the chiral ligand (*S*,*S*)-Naph-diPIM-dioxo-R **5** to afford (*R*,*S*)-**4** with a 77:23 enantiomer ratio (er) and its disastereomer with a 93:7 er in a 90:10 dr and in 81% yield (Scheme 2). Using *t*-Bu-BOX **6** as a ligand, which

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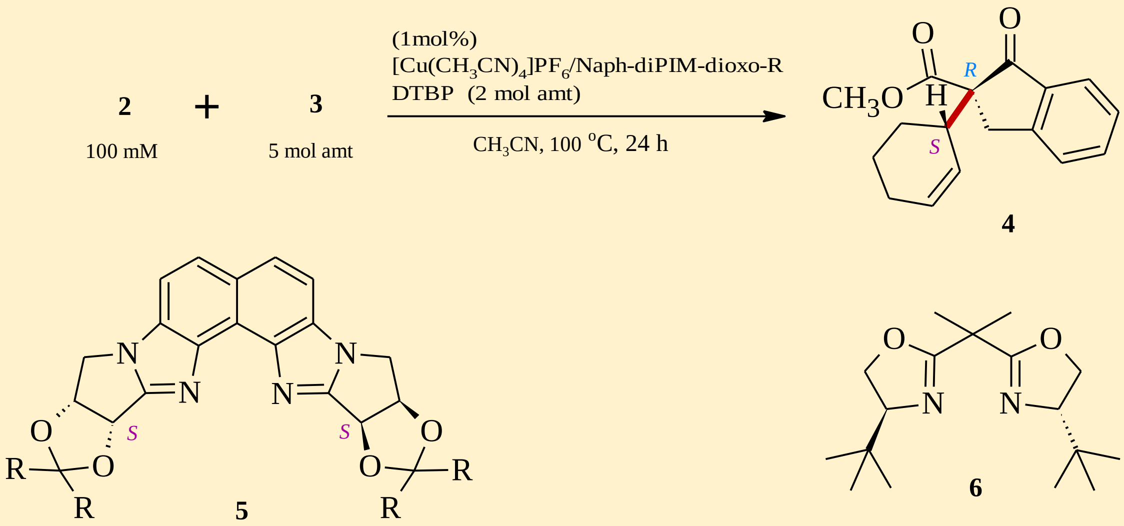
is known as the privileged chiral sp^{3}N bidentate ligand, was less effective than chiral Naph-diPIM ligand.



(*S*,*S*)-Naph-diPIM-dioxo-R

R = Me : 81% yield
90: 10 dr
er : 77:23 (major); 93:7 (minor)

R = *i*Pr : 73% yield
89:11 dr
er : 81:19 (major); 82:18 (minor)

t-Bu-BOX

52% yield
90:10 dr
er : 51:49 (major)
83:17 (minar)

Scheme 2 Asymmetric C-allylation of **2** with **3** catalyzed by cationic Cu(I) complex of chiral Naph-diPIM ligand and t-Bu-BOX ligand.

The operating mechanism is assumed to be a two-electron transfer mechanism or Cu(I)/Cu(II) redox.

Review

S. Tanaka, G. Ramachandran, Y. Hori, M. Kitamura, *Chem. Lett.*, **2018**, *47*, 1486–1489.

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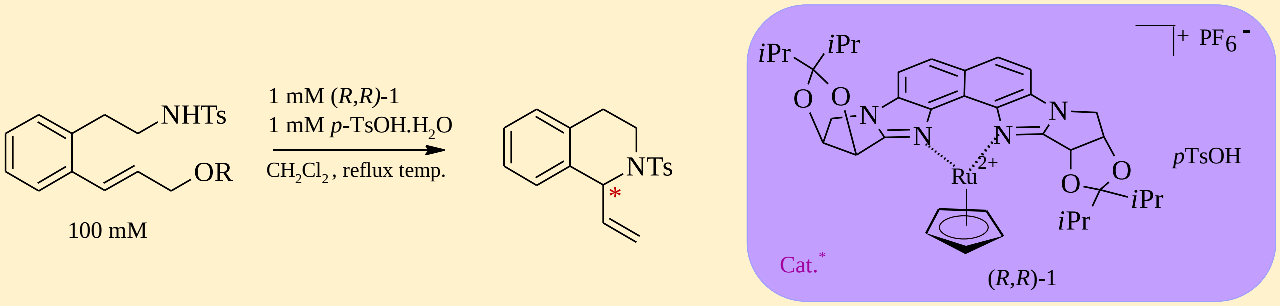
Expansion of the scope of Tsuji-Trost Reaction

A π-allyl donicity switch in catalytic asymmetric allylation has been demonstrated. This new deviation from Tsuji-Trost scope adapted a chiral CpRu(II)/*p*-TsOH combined catalyst and chemically stable allyl methyl ethers as π-allyl donors.

Conventional Tsuji-Trost-Pd chemistry operates under basic conditions. Expansion of the scope of this reaction paves the way in enhancing the scope of synthetic possibilities. In this context, Kitamura and co-workers demonstrated a chiral CpRu(II)/*p*-TsOH combined catalyst for asymmetric allylation that induced the π-allyl donicity of chemically stable allyl methyl ethers (ROMe) (Scheme).



Scheme catalytic asymmetric intramolecular allylation using allyl methyl ethers as π-allyl donors and a 1:1 molar ratio of (*R*,*R*)-1/*p*-TsOH combined catalyst.

CpRu(II)/*p*-TsOH combined catalyst exhibited an extraordinary high performance in asymmetric dehydrative C-, N-, and O- allylation. Such new deviation from Tsuji-Trost scope has changed the chemoselectivity profile and realized the highly enantioselective Tsuji-Trost-type C-, N-, and O-allylation, enhancing the flexibility in the retrosynthetic design of complex natural products.

Review

Y. Suzuki, S. Iwase, K. Hashimoto, S. Tanaka, M. Kitamura, *Chem. Lett.*, **2017**, 46, 1308–1310.

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“Pharaoh’s Snakes” for Fabricating Fe-/N-Doped Carbon Electrocatalysts

A novel and convenient technique is described for the preparation of high-performance Fe/N-doped carbon (Fe/N-C) electrocatalysts as potential alternatives to precious metal catalysts for the development of low-cost fuel cells and metal−air batteries.

Oxygen reduction reaction (ORR)/oxygen evolution reaction (OER) plays key roles in proton exchange membrane fuel cells and metal−air batteries that employ noble metal catalysts. Due to their high cost, limited resource, and poor durability impede their extensive applications, the development of efficient nonprecious metal catalysts as alternatives to noble metal catalysts is of great interest. In this regard, Shui and co-workers were inspired by the ancient chemistry and developed a facile fabrication method that based on the thermolysis of mercury thiocyanate, known as “Pharaoh’s snakes”, in which a small amount of precursors turn into a big snakelike foam in seconds upon heating. The method adapted eco-friendly precursors of sugar, soda, ferric nitrate, and melamine for an $Fe-N_x$/N-doped porous carbon.

Fabrication method

A mixture of sugar, melamine, and ferric nitrate were used as sources of C, N, and Fe, respectively, and ground uniformly with soda in an agate mortar. Then, the mixture was ignited with the aid of ethanol to form a long and snakelike black ash. The role of soda was to blow the molten sugar into the porous “snack” by releasing CO_2 upon heating (Figure). The growing process time was 10 s. Then, the black ash was pyrolized in a tube furnace under nitrogen atmosphere at 800, 900, or 1000 °C for 3 h to afford the electrocatalyst FeNC-*X* (*X*: pyrolysis temperature). The scanning electron microscopy (SEM)

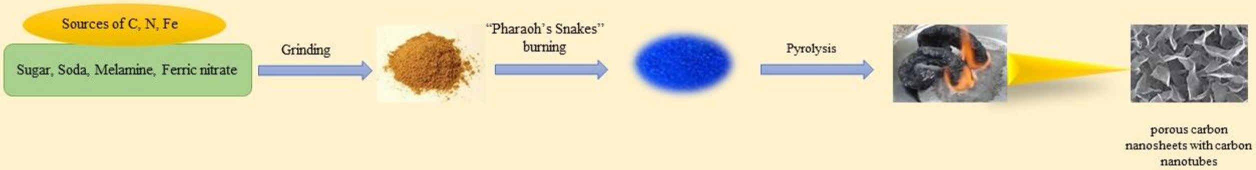

Figure Schematic illustration of the fabrication of 3D $Fe-N_x$/N doped nanosheets/nanotubes by the “Pharaoh’s snakes” method.

images of FeNC-1000 showed porous carbon nanosheets with carbon nanotubes.

Results

Among their findings were:

- The resultant Fe/N−C catalyst has a hierarchically porous structure, a large surface area, and uniformly distributed active sites.
- The optimized FeNC-1000 showed high activities toward ORR with a half-wave potential of 0.90 V [vs reversible hydrogen electrode (RHE)] more positive than the commercial Pt/C and OER comparable to that of RuO_2.
- In Zn−air cells, the FeNC-1000 cathode displayed a high open circuit potential (OCP) of 1.42 V and a specific capacity of 680 mA h g_{Zn}^{-1} as well as an excellent stability better than that of Pt/C. The discharge voltage of FeNC-1000-derived Zn−air cell was dropped to negative values after cycling 148 times, due to the passivation of the catalyst as the result of the generation of much zinc carbonate in the air atmosphere. To overcome this problem, they developed a regeneration method to revive the air electrode by washing the electrode with 6 M KOH.

$$ZnCO_3 + 2KOH \rightarrow K_2CO_3 + Zn(OH)_2\downarrow \qquad (1)$$

$$Zn(OH)_2 + 2KOH \rightarrow K_2ZnO_2 + 2H_2O \qquad (2)$$

The methodology showed the efficient utility of “Pharaoh’s snakes” in the fabrication of high-performance Fe/N-C electrocatalysts as potential alternatives to precious metal catalysts.

Review

G. Ren, L. Gao, C. Teng, Y. Li, H. Yang, J. Shui, X. Lu, Y. Zhu, L. Dai, *ACS Appl. Mater. Interfaces*, **2018**, *10*, 10778−10785.

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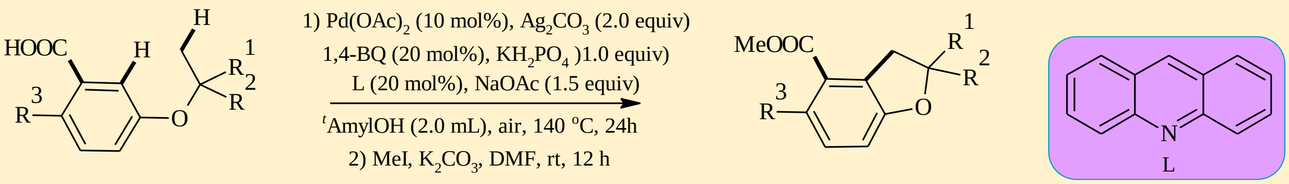
Oxidative Coupling of *sp*^{2} and *sp*^{3} Carbon-Hydrogen Bonds to Construct Carbon-Carbon Bonds

A versatile synthetic pathway is described for the intramolecular oxidative coupling between phenyl- and “inert” aliphatic carbon-hydrogen bonds to construct dihydrobenzofurans.

Benzo-fused scaffolds play key role in life science and material chemistry, which can be constructed through intramolecular cross-couplings or reductive couplings from two functionalized motifs. Shi and co-workers reported an efficient oxidative coupling protocol to prepare dihydrobenzofuran derivatives from phenyl alkyl ethers (Scheme).



Scheme. Synthesis of benzo-fused rings through oxidative coupling by ligand-manipulated tandem C-H activations

The adapted strategy based on ligand-manipulated tandem carbon-hydrogen activation. The weakly coordinated carboxylate was found to be effective directing group which upon manipulation provides Pd(II) complex followed by undergoing strain release of the palladacycle and Pd insertion into the aliphatic carbon-hydrogen bond.

The carboxylic acid group can be tranformed into a wide range of diverse functionalities, thus expanding the rang of the application of this pathway.

Review

J-L. Shi, D. Wang, X-S Zhang, X-L. Li, Y-Q. Chen, Y-X. Li, Z-J. Shi, *Nat. Communications*, **2017**, 8:238.