

Towards Green Environment and Sustainable Energy: Proposals for Reduction of Carbon Dioxide to Methanol

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Towards Green Environment and Sustainable Energy: Proposals for Reduction of Carbon Dioxide to Methanol

Atef Sobhy Iskander

Increasing levels of carbon dioxide in the atmosphere have raised the concerns over their negative impact on global eco-systems. Reduction of CO₂ and conversion to renewable fuels and valuable chemicals is a promising option to reduce the greenhouse-gas emissions. Among research efforts to address this challenge, hybrid porous materials have the capability to serve as fuel gas separation, capture and reversible storage. This contribution presents briefly the key hybrid porous materials that show potentials for gas adsorption and storage applications including the strategies of their synthetic routes in short. Moreover, two hypothetical proposals for hydrogenation of CO₂ to methanol, as a green and sustainable energy source, are described. These approaches based on a ternary catalytic system, and are Mg/CeO_x/ZnO and Cu/CeO_x/ZnO catalysts. The proposed mechanistic pathway to justify their performance is also presented.

Keywords: Hybrid materials, Carbon dioxide hydrogenation, CO₂ adsorption and storage, Methanol synthesis, Ceria.

1. Introduction

The current global energy and environmental challenges have raised increasing concerns over the role of carbon-based energy paradigm. How can the increasing level of carbon dioxide (CO₂) in the atmosphere be reduced? How can the increasing fuels demand of our society be fulfilled? Our society requires continuous renewable sources of energy that have no threats to our global eco-systems. Renewable sources of energy must be stored and transferable over space and time similar to that of fossil fuels. Ongoing research efforts to address these concerns have focused on many aspects to reduce the emission of CO₂ through capture; storage and conversion to methane (CH₄) or methanol (CH₃OH) as alternatives to fossil fuels.

The potential use of hydrogen (H_2) as an energy carrier, in principle, reduces or even eradicates CO_2 emissions at the point of use. Serious efforts have been achieved to invent new multi-functional materials that are quite efficient for fuel gas separation, capture and reversible storage as a way to reduce the threats of their emissions. Porous coordination polymers constructed from metal cation and cluster nodes linked by organic ligand linkers with regular architectures on the nanoscopic scale are an important domain of hybrid compounds that show high potential for such applications. This article highlights briefly the key hybrid porous materials that show potentials for gas adsorption and storage applications including the strategies of their synthetic routes in short. Moreover, novel hypothetical proposals for conversion of CO_2 to CH_3OH are described. These proposed approaches based a ternary catalytic system, and are $Mg/CeO_x/ZnO$ and $Cu/CeO_x/ZnO$ catalysts. The proposed mechanistic pathway to justify their performance is also presented.

2. Hybrid Porous Materials

Metal-Organic Frameworks (MOFs) attracted a significant interest owing to their high potential for multifaced applications ranging from optoelectronics and photonics to electrochemical and biomedical applications. The skeleton of MOFs contains organic part which has structural functions, and inorganic part which can provide specific functionalities. Their combination can allow the possibility to tailor the properties of the final materials through tuning the chemical nature, structure and ratio of both parts leading to three-dimensional framework that features outstanding properties.

The skeleton of most of the MOFs contains beside their components and the solvent, which acts as the main template, other inorganic or organic templates such as amines and quaternary ammoniums. These templates have strong electrostatic host-guest interactions, which energetically represent an important contribution to the lattice energy. While the solvents have weaker interactions with the skeleton leading to easily evolve the framework at low temperature, keeping the structure intact, and providing readily accessible porosity. Furthermore, the existence of both inorganic and organic components in the framework allows hydrophilic and hydrophobic parts to coexist within the pores, which may have a positive impact on the adsorption properties. MOFs have the ability to allow modularity for a given structural type and also within it which can create a new type of porous hybrid.¹⁻⁴

3. Synthetic Approaches of Hybrid Organic/Inorganic Nanoparticles

The surface of inorganic nanoparticles can be tuned by organic particles to modify their properties or by polymers to produce hybrid materials with new unique properties. The interaction between the organic and inorganic nanoparticles can take place either by covalent or noncovalent binding. The synthetic pathway determines the properties of the resulting species. In a general sense, the organic linker is topologically neutral during the process, while the nuclearity and dimensionality are determined by the inorganic part which depends on the synthesis parameters and will shape the final structure. The most important chemical parameters of the syntheses of MOFs are pH (mostly acidic), concentration, and temperature. The temperature influences greatly the coordination of the metallic particles, the nuclearity and /or the dimensionality of the inorganic subnetwork. This leads to a new field of potential applications together with their properties of potentially unlimited pore sizes and surface areas. For example, the increase of temperature enhances nuclearity followed by a change into chains then layers of inorganic polyhedral under fixed other parameters.

3.1. Noncovalent Interaction

The interaction between a charged particle and the charged surface of an inorganic particle takes place via the electrostatic forces. Such coatings processes can be achieved through: i) direct addition, in which the opposite charged particles combine together; ii) desalting, in which both particles are dispersed within a media in the presence of salt ions that stabilize the particles from interaction. The removal of the salt leads to the formation of an ordered aggregation; iii) layer-by-layer, which the deposition leads to the formation of homogeneous coating featuring attractive hierarchical morphologies.⁵

The layer-by-layer process is accomplished by the addition of one charge particles into a concentrated suspension of the oppositely charged particles forming a shell of opposite charge on the particle surface. Such techniques are used in biomedical applications. For example, ZnO nanorod-based hybrid nanoparticles prepared with cores made of ZnO/GeO₂, ZnO/CdS, and ZnO/Ag at room temperature.⁶

3.2. Covalent Interaction

The coating of inorganic particles surfaces with functional groups can be achieved through conventional chemical reactions. Among these reactions, “click chemistry” is a powerful method in grafting polymer chains to the surface of the particles under relatively mild conditions.⁷ For example, the grafting of polystyrene onto the surface of titania nanoparticles is accomplished via “click chemistry”. The titania surface was prepared by phosphonate coupling followed by the attachment of polystyrene chains to the surface of the modified particles via click chemistry.⁸

3.3. Hierarchical Hybrid Nanoparticles

The interaction of performed inorganic and organic nanoparticle is a heterocoagulation technique which allows the interaction and aggregation of the particles to produce hybrid nanoparticles with complex shapes and great morphological control. This approach can be used to the modified particle surfaces of both types with oppositely charged groups to allow a homogeneous coating via electrostatic interaction, or to functionalize the nanoparticles with complementary groups in order to allow them to react covalently. For example, the preparation of raspberry-like particles by heterocoagulation oppositely charged colloids is accomplished using an organic core of cross-linked polystyrene particles functionalized at the surface with amino groups and three different types of inorganic particle: anionic silica, gold precipitated in the presence of trisodium citrate dehydrate, and maghemite precipitated in the presence of poly(acrylic acid) and diethylene glycol.⁹ The polystyrene particles were added dropwise to a suspension of inorganic nanoparticles. The adsorbed inorganic nanoparticles located within the electrostatic double layer of the polymer particle serve as multivalent counter-ions.

4. Carbon Dioxide Adsorption & Storage

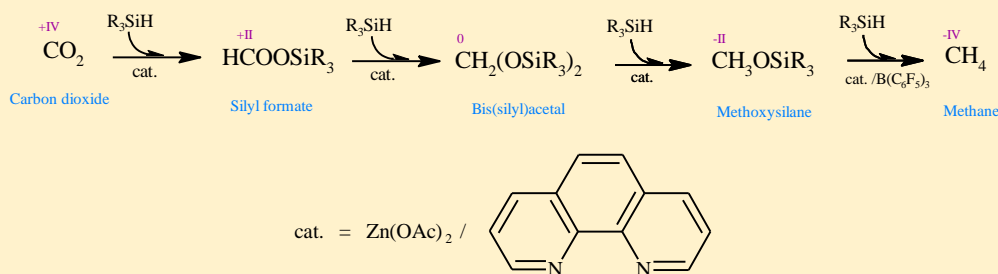
MOFs have the ability to adsorb large amounts of gases within the cages of their porous. Many MOFs were developed for CO₂ and CH₄ storage. Generally, CO₂ is more adsorbed than CH₄ which may be related to the large quadrupolar moment for CO₂ ($-1.4 \times 10^{-35} \text{ C m}^2$).¹⁰ Such moment does not exist with CH₄. In fact, this moment induces specific interactions with adsorbents, which will offer different behaviors for the adsorption isotherms depending on the host structure. In view of adsorption isotherms, MOF-177 and MIL-101 are considered as good adsorbers owing to their large pores, *i.e.* SSA: 4500 m² g⁻¹, 11 x 17 Å pores for MOF-177¹¹ and SSA: 5900 cm² g⁻¹, 29 and 34 Å diameters for MIL-101¹². MOF-177 adsorbs 33.5 mmol g⁻¹ at 16 bar and 33.5 mmol g⁻¹ at 40 bar, while MIL-101 adsorbs 16 mmol g⁻¹ at 16 bar and 40 mmol g⁻¹ at 70 bar, which equivalents to ten times the amount of pure CO₂ in a container at the same pressure.

The chromium terephthalate MIL-101 presented a pronounced performance for selective gas adsorption, separation, and energy storage. This is related to its large pores (29 and 34 Å) and BET surface area (> 3000 m² g⁻¹) with a huge cell volume (approximately 702000 Å³) together with the coordinatively unsaturated open metal sites.¹³

Selective hydrogenation of CO₂ to ethanol was achieved through cooperative Cu^I sites on Zr₁₂ cluster of MOF with assistance of an alkali cation.¹⁴ The Cs⁺-modified MOF produced ethanol, in 10 hours, with > 99% selectivity and turnover number (based on all Cu atoms) of 4,080 in supercritical CO₂, with 30 MPa of CO₂ and 5 MPa of H₂ at 80 °C, or a turnover number of 490 at 2 MPa of CO₂/H₂ (1/3) and 100 °C.

Various catalysts have been developed for the conversion of CO₂ to CH₃OH. For instance, electroreduction of CO₂ to CH₃OH was accomplished by nanostructuring pulse-depositing Zn dendrites onto Ag foams, which enhanced the reduction with Faradaic efficiency and current density values up to 10.5% and -2.7 mA cm⁻², respectively.¹⁵

Another interesting approach was accomplished by zinc catalyzed hydrosilylation of CO₂ to CH₄.¹⁶ A turnover number of 815000 was realized using Zn(OAc)₂ with 1,10-phenanthroline as a ligand (Scheme 1).



Scheme 1. Carbon dioxide hydrosilylation to methane catalyzed by Zn(OAc)₂ with 1,10-phenanthroline.

5. Proposals for Reduction of Carbon Dioxide to Methanol

Inspired by the great achievements in this field, I offer two hypothetical proposals for the conversion of CO₂ to CH₃OH as a good fuel, given the abundance of CO₂ in the atmosphere and sustainable carbon resources. Methanol is a renewable energy source that can be used as transportation fuel. In addition, methanol can be transformed to olefins and other high value-added chemicals.

In order to meet the requirements of large-scale production of methanol, there is a need to an efficient catalyst that enables the hydrogenation of CO₂ to methanol with high selectivity and stability. There are many good metal catalysts developed for such conversion such as Cu/ZnO/Al₂O₃, Cu/ZrO₂, Pd/ZnO, Ni(Pd)-Ga, Cu(Au)/CeO_x/TiO₂, ZnO-ZrO₂ and In₂O₃. However, these catalysts suffer from the low selectivity caused by reverse water-gas shift reaction and the rapid deactivation caused by water. Such deactivation enhances, for example, the sintering of Cu active component during the hydrogenation process.¹⁷ As a preliminary step to design a catalyst for such conversion, the question that arises is what are the dominant factors affecting the hydrogenation of CO₂? A crucial factor in the enhancement of the catalytic performance is the interaction between metal and metal oxide.¹⁸ The strong interaction creates a large number of active sites for CO₂ and H₂ adsorption, leading to the maximum yield of methanol. Furthermore, the strong interaction can reduce the transport distance for hydrogen atom spillover¹⁹ and activation barriers for CO₂ hydrogenation to CH₃OH.^(19,20) Besides, the large surface area of the metal can lead to the extent of hydrogen spillover to the metal oxide, as well as the presence of enough oxygen vacancies which can lead to large amount of intermediates formed that could provide the sites for CO₂ hydrogenation.²¹

In view of these factors, I hypothesize a composite of nanostructured catalyst Mg/CeO_x/ZnO for CO₂ hydrogenation to methanol. Another approach is proposed and is a ternary system of Cu/CeO_x/ZnO.

Magnesium has the dynamic activities of hydrogen dissociative adsorption on it, and demonstrates good activity for an efficient hydrogen storage.²² On the other hand, Cu and Ag based catalysts produce mainly CH₃OH.²³ Each metallic catalyst shows, on its own, limited catalytic activity, thus, supported metal catalyst shows enhanced catalytic properties. Composite support contains two or more oxides has been found to enhance the catalytic performance such as reducibility, active metal dispersion and stability. For example, enhanced improvement was observed in dispersion and reducibility for Ni based catalyst in ZrO₂-Al₂O₃ composite, which was attributed to ZrO₂ inhibiting the incorporation of Ni species in the lattice of γ -Al₂O₃.²⁴ It is therefore assumed that a composite of CeO_x/ZnO can promote Mg or Cu species that lead to the improvement in CO₂ conversion and CH₃OH selectivity.

Ceria (CeO₂) showed a high catalytic performance for hydrogenation reactions due to its higher specific surface area and its ability to promote the low-temperature reducibility. Cerium(III) oxide (Ce₂O₃) has the

potential to decrease the energetic barrier for the hydrogen dissociation compared to CeO_2 . Ce_2O_3 surfaces lead to a heterolytic product with hybrid species more stable than the homolytic product, which is the opposite behavior found in CeO_2 .²⁵ Such performance reflects its ability to dissociate hydrogen better than CeO_2 resulting in the formation of oxygen vacancy on its surface.

6. Proposed Mechanism for Carbon Dioxide Hydrogenation to Methanol

In order to justify these hypothesized catalytic approaches, I suggest a mechanistic pathway in the light of the literature. Gaseous hydrogen dissociatively adsorbed on the Mg^0 (Cu^0) forming hydrogen atoms, and then the hydrogen atoms spillover to the ceria CeO_x through the interface between Mg^0 (Cu^0) and CeO_x leading to a change of the stoichiometry from CeO_2 to Ce_2O_3 . An increase of the Ce_2O_3 level can gradually lead to the rise of basisty (the ratio of Mg or Cu to ZnO) of the composite, which is thermodynamically favorable to the enrichment and participation of ceria-containing Mg or Cu species. Gaseous CO_2 adsorbed on the oxygen vacancies of CeO_x forming a carbonate species. Then the carbonate species react with the adjacent hydrogen atoms forming dioxomethylene followed by methoxy formation and water. The methoxide species react with water to yield methanol and hydroxide groups. Finally, the hydroxide group react with hydrogen atoms to give water (Figure 1).^{26,27}

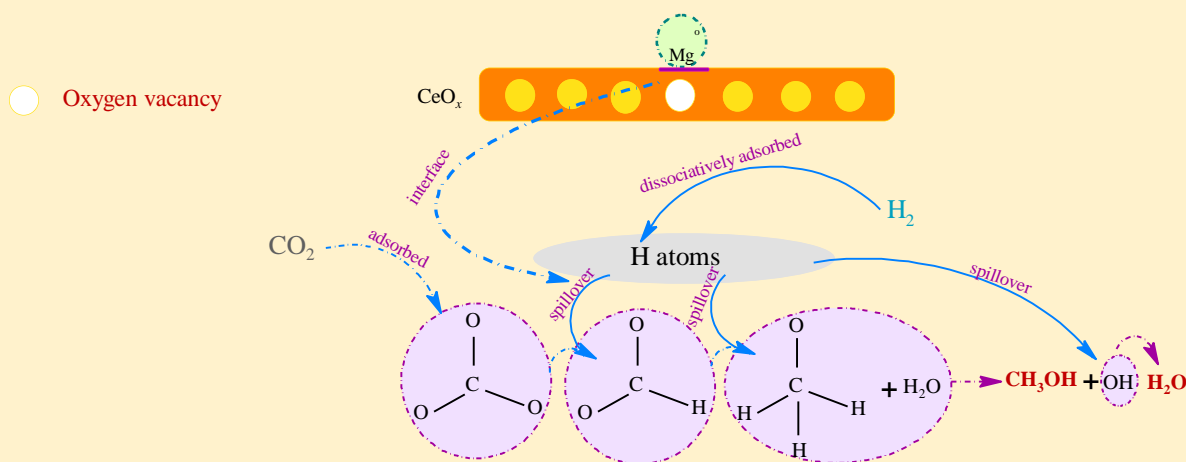


Figure 1. Reaction pathway of CO_2 hydrogenation to methanol over CeO_x catalysts.

Upon changing the stoichiometry from CeO_2 to Ce_2O_3 , a productive H_2 -evolving CeO_x oxidation takes place due to the participation of OH groups (Figure 2).²⁸ This is related to the effective splitting of water by highly reduced cerium oxide. The effective oxidation of highly reduced CeO_x by water to the next-neighbor oxygen vacancies allows for effective incorporation of water via formation of OH groups.

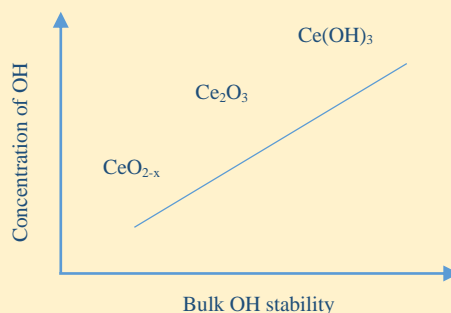


Figure 2. Schematic illustration of the participation of OH groups.

7. Conclusion

The progress in the field of hybrid porous materials is enormous due to the quasi-infinity of possible combinations between organic and inorganic moieties, and the ability to chemically tailor the composition, structure and functionalities of their moieties which pave the way to design multifunctional materials.

Biogas upgrading through direct CO₂ hydrogenation to methanol could be a competitive option rather than disposal, which could realize power-to-gas for renewable energy storage and could have a wide range of important industrial applications. In this article, I hypothesize two approaches for the conversion of CO₂ to methanol based on a ternary of magnesium (copper) catalytic system, which may be highly fruitful. Mg-containing catalysts offer good chance for tailored design of pore structure, and high hydrogen uptake. In addition, ceria, as promoters, may further enhance the catalyst system by improving H₂ and CO₂ activation, as well as catalyst's reducibility, active metal dispersion and stability. Hence, tuning the morphology of ceria may provide a good tool to produce well-defined nanostructured catalyst for such conversion at low temperatures. Further, nanosized magnesium (copper) particles may result in a high catalytic activity due to the strong interaction between CeO_x and Mg (Cu), promoting the hydrogenation of formate species, which may believe to be the rate-limiting step. The hypothesized approaches in this article would enrich the knowledge in understanding the fundamental features of the catalytic performance and in designing rational catalyst.

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

Atef S. Iskander

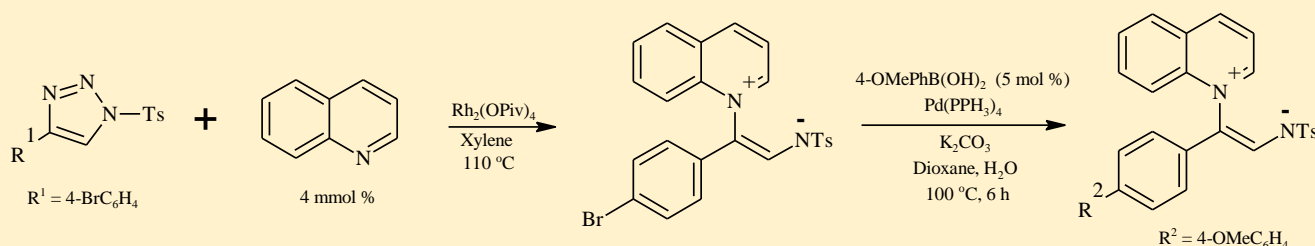
Managing Director / Founder

Novel Synthesis of Diazapine Derivatives

A novel synthetic strategy based on one-pot [5+2] cycloaddition of *N*-aromatic zwitterion with in-situ generated ketenes to form 1,5-diazapine derivatives is described.

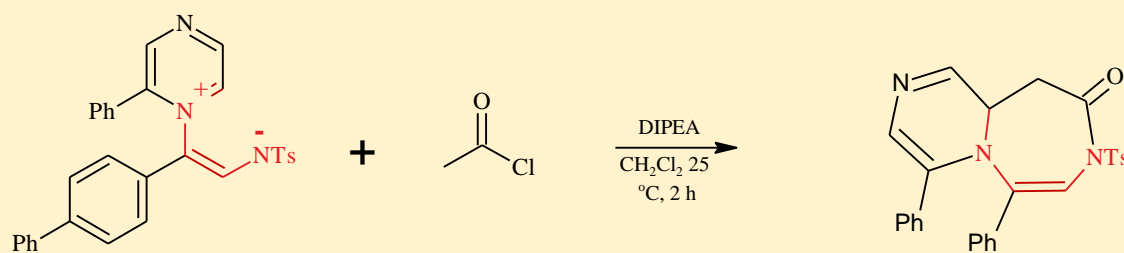
Dipolar cycloadditions are important approaches for the synthesis of heterocyclic and polycyclic molecules, which constitute the core building blocks of a wide range of natural products and play an important role in medicinal chemistry. In this context, Lee and co-workers reported a series of *N*-aromatic zwitterions which could be employed in cycloaddition for the preparation of diazapine derivatives.

These *N*-aromatic zwitterions were generated by rhodium(II) catalyzed reaction between 1-sulfonyl-1,2,3-triazoles and *N*-aromatic compounds, such as quinolines and isoquinoline, which could further be employed in palladium-catalyzed coupling reactions such as the Suzuki reaction to amplify their diversity (Scheme 1).



Scheme 1. Functionalization of *N*-aromatic zwitterion.

The prepared *N*-aromatic zwitterions were used as a five-atom synthons to form [5+2] dipolar cycloadditions with ketene, which was generated in-situ from acetyl chloride, affording 1,5-diazapine derivatives smoothly (Scheme 2).



Scheme 2. [5+2] Cycloaddition of N-aromatic zwitterions and ketene.

The calculated values of NICS(0) and the angle of twist on the obtained zwitterions confirmed the strong relationship between structure and stability. This methodology will find a broad application in medicinal chemistry.

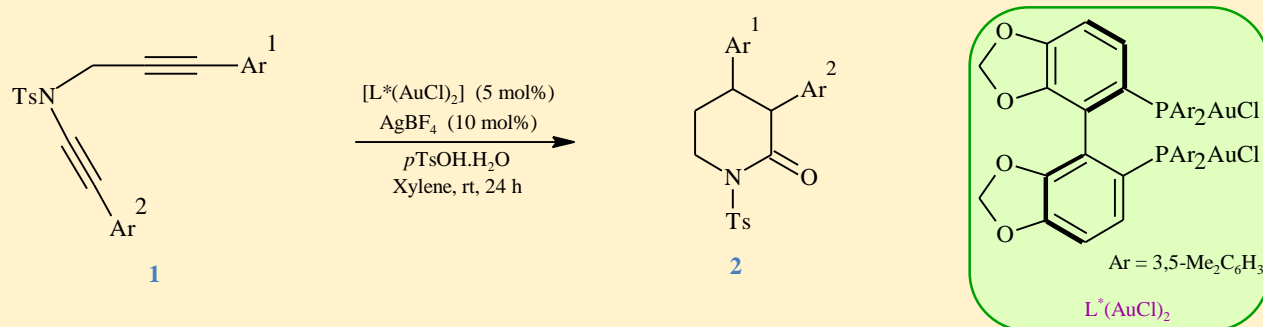
Review

J. Y. Lee, J. Kim, J. H. Lee, H. Hwang, E J. Yoo, *Asian J. Org. Chem.*, **2019**, 8, 1654–1658.

Enantioselective Gold(I)-Catalyzed Hydrative Cyclizations of Ynamides

A new methodology is described for the preparation of high levels of stereocontrol of *N*-tosyl-3,4-dihydropyridin-2(1*H*)-ones. The synthetic route is accomplished via the enantioselective gold(I)-catalyzed hydrative cyclizations of *N*-propargyl-ynamides and water in the presence of *p*-toluenesulfonic acid.

In view of the growing interest in the synthesis of chiral nitrogen-containing heterocycles, Febvay and co-workers have targeted enantioselective variants of the hydrative cyclizations of the *N*-tosyl-*N*-propargyl-ynamides **1** and *p*-toluenesulfonic acid as a promoter using (3,4-Me₂C₆H₃-SEGPHOS)(AuCl)₂ [L^{*}(AuCl)₂] chiral catalyst in combination with silver tetrafluoroborate (AgBF₄) as the chloride removal agent in xylene as a solvent. The reaction produced the desired 3,6-dihydropyridinone **2** (Scheme).



Scheme 1. Enantioselective Gold(I)-Catalyzed Hydrative Cyclizations of Ynamides

Different substituted derivatives were prepared in moderate to good yields and with up to 94:6 er. This contribution presents an unprecedented gold-promoted cyclization route.

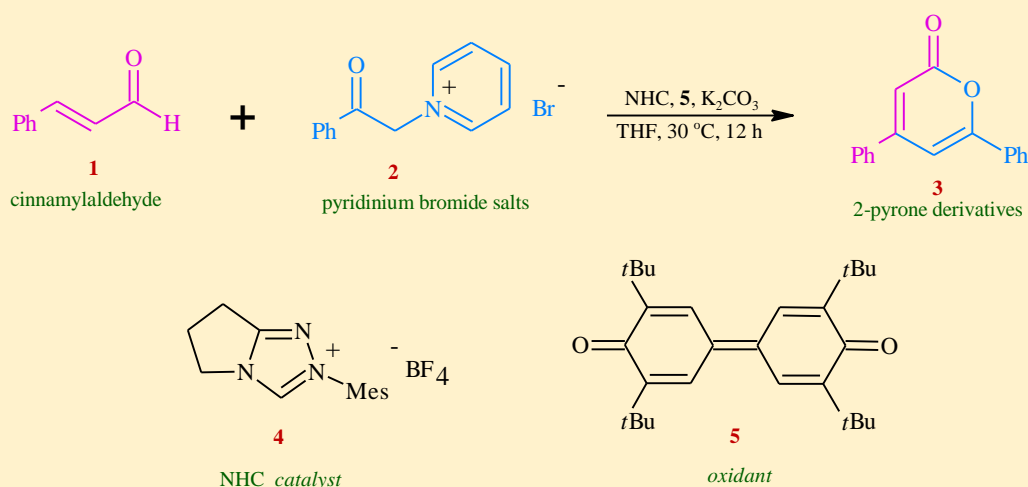
Review

J. Febvay, Y. Sanogo, P. Retailleau, M. P. Gogoi, A. K. Sahoo, A. Marinetti, A. Voituriez, *Org. Lett.*, **2019**, *21*, 9281-9285.

Quick Access to 2-Pyrones

Quick synthetic pathway to 2-pyrones is described. A carbene-catalyzed oxidative [3+3] cycloaddition reaction between enals and 2'-pyridinium acetophenone bromide salts as precursors of nitrogen ylides was achieved to afford 2-pyrone products in moderate to excellent yields.

Substituted 2-pyrones constitute interesting building blocks for the synthesis of functional molecules owing to their multiple reaction sites. The team of Chi reported an efficient access to 6-membered lactone **3** via the reaction of enals **1** with pyridinium bromide salts **2** using *N*-heterocyclic carbene (NHC) **4** as a catalyst in the presence of an oxidant **5** and K₂CO₃ as a base in THF to afford substituted 2-pyrones in moderate to good yield (Scheme).



Scheme. A carbene-catalyzed oxidative [3+3] cycloaddition reaction between enals and nitrogen ylide.

The inexpensive and easily prepared 2'-pyridinium acetophenone bromide salts are employed as the nitrogen ylide precursors. Both electron-withdrawing and electron-donating groups are well tolerated on the benzene rings of the pyridinium bromide salts under this catalytic process.

Review

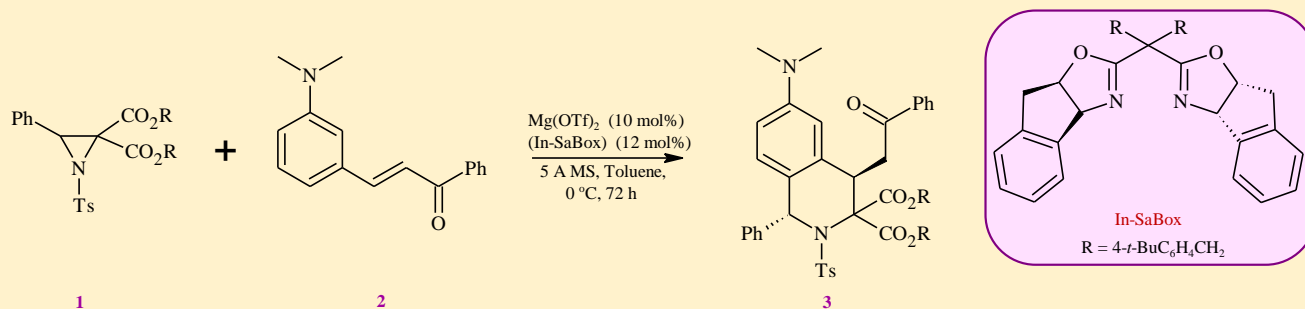
P. Zheng, C. Li, C. Mou, D. Pan, S. Wu, W. Xue, Z. Jin, Y. R. Chi, *Asian J. Org. Chem.*, **2019**, 8, 1067-1070.

Construction of Highly Functionalized Enantioriched Tetrahydroisoquinolines

Synthesis of highly functionalized tetrahydroisoquinoline derivatives is outlined. The route is accomplished by a diastereo and enantioselective catalytic [3+3] cycloaddition of donor-acceptor aziridines with *N,N*-dialkyl-3-vinylanilines catalyzed by $\text{Mg}(\text{OTf})_2$ / bis-oxazoline.

In view of the unique structural features of chiral tetrahydroisoquinolines and their important biological activities, Kim *et al.* reported a new synthetic approach for the preparation of these compounds via asymmetric catalytic [3+3] cycloaddition of donor-acceptor aziridines.

A wide range of donor-acceptor aziridines **1** reacted with *m-N,N*-dimethylaminophenyl α - β -unsaturated phenyl ketone **2** using $\text{Mg}(\text{OTf})_2$ and a side armed indane-derived bisoxazoline (In-SaBox) ligand as catalyst, which the side arm group plays an important role in the enantiomeric control of this reaction, to afford highly functionalized tetrahydroisoquinoline derivatives **3** (Scheme).



Scheme . Synthesis of highly functionalized tetrahydroisoquinoline derivatives.

The cycloaddition reaction proceeded also well with 3-(*m-N,N*-dimethylaminophenyl)acrylates as well as donor-acceptor *N*-tosylaziridines to afford the products in good yields and with high diastereo- and enantioselectivities up to 30:1 d.r., 95:5 er.

Review

S. Kim, S-G. Kim, *Asian J. Org. Chem.*, **2019**, *8*, 1621-1625.