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甲烷是個有趣的分子，它是最小的烷類，但卻有烷類分子間最強的 C-H 鍵，使得它較難被活化利用。它是比較環保的石化燃料，但甲烷本身引起的溫室效應，卻又 22 倍於二氧化碳。最近 10 年，由於美國頁岩氣(大部份是甲烷，但 wet shale gas 內含 10%~20% C₂-C₄ 烷類)的開採成功，產量迅速提昇，一場能源革命正在悄悄的上演，對石化產業也會產生相當的衝擊。另外，全球尚有蘊藏量龐大的可燃冰(天然氣的水合物，大約 80% 甲烷 20% 二氧化碳)，台灣墾丁和日本外海，近來亦有發現。上述的發展，提供化學家們開發新資源的機會和挑戰，所以此次通訊包括了幾篇轉化甲烷的論文:(I) Green Chemistry Meetings (pp. 1), (II) On-Line Seminar (pp. 2), (III) Books on Solar Fuels (pp.3) (IV) Developments in Green Chemistry (pp.4), and (V) A Few Papers on Methane Activation (pp. 16).

I. Green Chemistry Meetings:

- (1) [10th Green Chemistry Conference](#), “Economic Growth and Sustainability through Green Chemistry”, November 5-7, 2013, Barcelona, Spain
- (2) [4th Asia-Oceania Conference on Green and Sustainable Chemistry \(AOC-4 GSC\)](#), November 2-6, 2013, New Taipei City Hall, Taiwan.
- (3) [Ecochem International Conference & Exhibition on Sustainable Chemistry & Engineering](#), November 19-21, 2013, Basel, Switzerland
- (4) [Nanosafety 2013](#), November 20 – 22, 2013, Saarbrücken, Germany
- (5) [International Workshop on Green Initiatives in Energy, Environment and Health](#), December 2-3, 2013, Delhi, India
- (6) [3rd Industrial Green Chemistry World \(IGCW\)](#), “Profitability from Industrial Green Chemistry and Engineering”, December 4-6, 2013, Mumbai, India
- (7) [247th ACS National Meeting & Exposition](#), “Chemistry & Materials for Energy”, March 16-20, 2014, Dallas, Texas, USA

- (8) [2nd International Conference on Clean Energy\(ICCES2\)](#), April 13–16, 2014, Qingdao, China
- (9) [Mechanochemistry: From Functional Solids to Single Molecules](#), May 21 - 23, 2014, Montreal, Canada
- (10) [18th Annual Green Chemistry & Engineering Conference](#), "Reimagining Chemistry, Building Our Future", June 17-19, 2014, North Bethesda, Maryland, USA
- (11) [Gordon Research Seminar on Green Chemistry](#), "Applications for Sustainable Future", July 26-27, 2014, Hong Kong, China
- (12) [Gordon Research Conference on Green Chemistry](#), "Industrial Successes and Challenges", July 27- August 1, 2014, Hong Kong, China

II. On-line Seminar:

- (13) ACS Webinars - [Green chemistry Education, Charting a Course for the Future](#) (此則信息由中研院化學所趙奕娣教授提供)

Technologies that lower our ecological footprint are essential for sustainable development. Green chemistry is an important part of this movement and is imperative to green the chemistry curriculum. Join Dr. Michael Cann (Prof. of Chemistry, University of Scranton) and Dr. Joe Fortunak as they look at why we need green chemistry and green chemistry education, its current state, where we need to go and how to get there.

- (14) 今年的 [ACS Summer School on Green Chemistry and Sustainable Energy](#) 的演講投影片上網了。(此則信息由中研院化學所趙奕娣教授提供)

講題如下:

[Greener Solvents](#)

[Choosing the Greenest Synthesis](#)

[Eco-Innovation and Product Design](#)

[Entrepreneurship](#)

[Energy Applications of Ionic Liquids](#)

[Greening Fossil Fuels](#)

[Green and Sustainable Chemistry by Design](#)

Design and Implementation of a Greener Lab Curriculum

Green Chemistry: Principles and Practice

Pine Chemicals: Sustainability and Innovation

III. Books on Solar fuels:

(15) Solar Energy Conversion - Dynamics of Interfacial Electron and Excitation Transfer

Piotr Piotrowiak (Editor), RSC Publishing, Copyright: 2013, ISBN: 978-1-84973-387-8,
Format: Hardback

The importance of developing new, clean and renewable sources of energy will continue to grow in the foreseeable future and so will the need for the education of researchers in this field of research. The interest and challenges of the field continue to shift from simple homogeneous solutions to increasingly more complex heterogeneous systems and interfaces. Over the past decade there have been numerous theoretical and experimental breakthroughs many of which still exist only in the primary literature. The aim of this book is to gather in one volume the description of modern, sometimes exploratory, experimental and theoretical techniques applied to the dynamics of interfacial electron and electronic excitation transfer processes studied in the context of solar energy conversion. The intended treatment will be fundamental in nature and thus applicable to a broad range of hybrid photovoltaic and photocatalytic materials and interfaces. The book will focus on the dynamic aspects of the electron injection, excitation and carrier relaxation processes, as well as coherence effects, which continue to provide the impetus and the greatest challenge for the development of new methodologies.

(16) Solar Hydrogen

Mario Pagliaro, Athanasios G Konstandopoulos (authors), RSC Publishing, Copyright:
2012, ISBN: 978-1-84973-195-9, eISBN: 978-1-84973-317-5,
DOI: 10.1039/9781849733175

Renewable hydrogen produced using solar energy to split water is the energy fuel of the future. Accelerated innovation in both major domains of solar energy (photovoltaics and concentrated solar power) has resulted in the rapid fall of the solar electricity price, opening the route to a number of practical applications using solar H₂. New thermochemical water splitting using concentrated solar power (CSP) as well as CSP

coupled to electrolysis has the potential to convert and store solar energy into clean hydrogen using a tiny fraction of the world's desert area to meet our present and future global energy needs. Photovoltaics, in turn, has the versatility required for supporting the creation of a distributed energy generation infrastructure in developing countries especially now that the price of PV solar electricity has fallen to unprecedented low levels. In all these cases, solar H₂ will be used to store energy and release it on demand either for fuel cells (to power homes and boats) or internal combustion engines and turbines (for powering cars, trucks and in thermoelectric power units). This book on solar hydrogen is unique in its field and is a timely treatment of a hot topic in industry, academic, political and environmental circles. With reference to many examples as well as to new technologies, this accessible book provides insight into a crucial technology for our common future and numerous colour pictures contribute to the book's readability. Written by experts in the field who are engaged at the forefront of research, the book supplies readers with last minute insight from the frontiers of research. The book will be of interest to Politicians, solar PV companies, hydrogen and sustainability researchers, environmentalists, managers in the automotive and nautical industries, undergraduate and graduate students in physics, chemistry, energy and materials science.

(17) [Solar Fuels](#)

Themed issue in Chemical Society Reviews ([Chem. Soc. Rev., 2013, Issue 5](#)). Find more information in the [Editorial](#) by Siddharth Dasgupta, Bruce S. Brunshwig, Jay R. Winkler and Harry B. Gray.

(18) [Recent Advances in Solar Energy Conversion and Utilization](#)

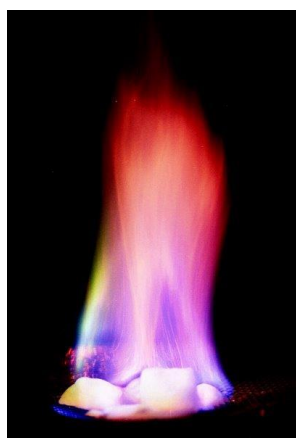
This is a themed issue containing articles from the journals Energy & Environmental Science, Physical Chemistry Chemical Physics (PCCP) *and* RSC Advances, and guest edited by Ranjit Koodali and Velu Subramani.

IV. Developments in Green Chemistry:

(19) [ACS News Service Weekly PressPac \(August 28, 2013\): Using a form of ice that burns to make potable water from oil and gas production](#)

Read the article: Increasing Gas Hydrate Formation Temperature for Desalination of High Salinity Produced Water with Secondary Guests,

In the midst of an intensifying global **water crisis**, scientists are reporting development of a more economical way to use one form of the “ice that burns” to turn very salty wastewater from fracking and other oil and gas production methods into water for drinking and irrigation. The study on the method, which removes more than 90 percent of the salt, appears in the journal *ACS Sustainable Chemistry & Engineering*. Yongkoo Seol and Jong-Ho Cha explain that salty wastewater is a byproduct of oil and gas production, including hydraulic fracturing, or fracking. These methods use water and produce as a byproduct almost 10 barrels of salty water for every barrel of oil. That water could help people in water-stressed regions. But it can't be desalinated economically with traditional methods. Seol and Cha knew that an alternative called “gas hydrate desalination” showed promise. A gas hydrate consists of only water and a gas such as methane, the stuff of natural gas. Thus, when hydrates form, salts and other impurities are left behind. When the hydrate breaks down, the gas and pure water are released. However, forming the gas hydrate used in desalination required costly chilling of the water to 28 degrees Fahrenheit. Seol and Cha sought to develop a less costly version of the method, which involves a variation on methane hydrates, chunks of ice retrieved from deep below the sea that burst into flame when brought to the surface. They describe development and laboratory testing of a new type of gas hydrate desalination technique. They formed the hydrates from water and carbon dioxide with the gases cyclopentane and cyclohexane, which made the method work more efficiently. It removed more than 90 percent of the salt compared to 70 percent with the previous gas hydrate technique. And the process works at near-room temperature, reducing the need for chilling.

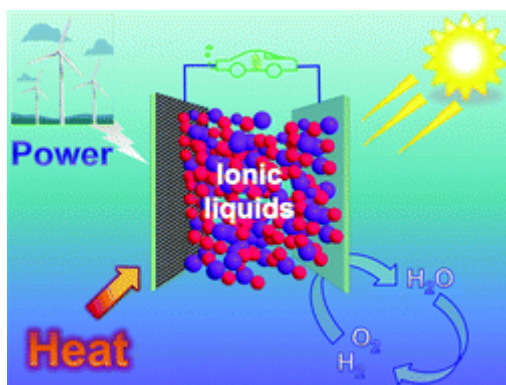


(20) Energy applications of ionic liquids

Energy Environ. Sci., 2013, Advance Article

DOI: 10.1039/C3EE42099J

Ionic liquids offer a unique suite of properties that make them important candidates for a number of energy related applications. Cation – anion combinations that exhibit low volatility coupled with high electrochemical and thermal stability, as well as ionic conductivity, create the possibility of designing ideal electrolytes for batteries, super-capacitors, actuators, dye sensitised solar cells and thermo-electrochemical cells. In the field of water splitting to produce hydrogen they have been used to synthesize some of the best performing water oxidation catalysts and some members of the protic ionic liquid family co-catalyse an unusual, very high energy efficiency water oxidation process. As fuel cell electrolytes, the high proton conductivity of some of the protic ionic liquid family offers the potential of fuel cells operating in the optimum temperature region above 100 °C. Beyond electrochemical applications, the low vapour pressure of these liquids, along with their ability to offer tuneable functionality, also makes them ideal as CO₂ absorbents for post-combustion CO₂ capture. Similarly, the tuneable phase properties of the many members of this large family of salts are also allowing the creation of phase-change thermal energy storage materials having melting points tuned to the application. This perspective article provides an overview of these developing energy related applications of ionic liquids and offers some thoughts on the emerging challenges and opportunities.

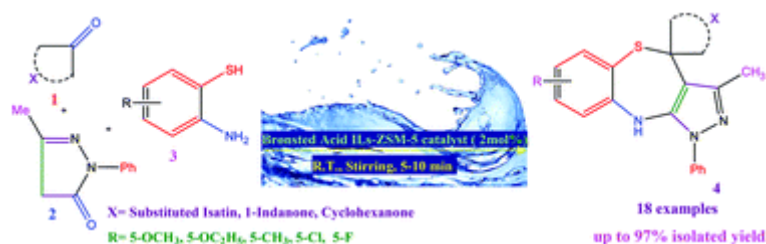


(21) Ionic liquid confined zeolite system: an approach towards water mediated room temperature synthesis of spiro[pyrazolo[3,4-*e*]benzothiazepines]

Green Chem., 2013,15, 2885-2894

DOI: 10.1039/C3GC40553B

A novel ionic liquid confined ZSM-5 zeolite catalyst system has been developed using different ionic liquids confined within a mesoporous ZSM-5 zeolite; their catalytic activity has been tested in aqueous media at room temperature for the greener synthesis of spiro[pyrazolo[3,4-*e*]benzothiazepine] analogues in higher yield with shorter reaction time for the first time. Recyclability of the novel catalyst system was also studied which resulted in no loss of their catalytic activity in up to five cycles making the whole system industrially viable.



(22) Conversion of glucose and cellulose into value-added products in water and ionic liquids

Green Chem., 2013,15, 2619-2635
DOI:10.1039/C3GC41141A

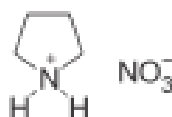
Lignocellulosic biomass contains about 45% cellulose. Conversion of cellulose and cellulose-derived glucose into value-added chemicals and liquid fuels benefits sustainable development of our society and has received much attention. Water and ionic liquids (ILs) are two kinds of green solvents. The unusual properties of the green solvents provide some unique advantages for efficient and greener conversion of cellulose and glucose, which have been studied extensively. This review discusses mainly the recent progress in the conversion of glucose and cellulose in water or ILs by oxidation, hydrogenation, and dehydration reactions. An outlook is presented in the last part of the article to highlight the challenges and opportunities related to this interesting area of great importance.



(23) How safe are protic ionic liquids? Explosion of pyrrolidinium nitrate,

Green Chem., 2013, Advance Article
DOI:10.1039/C3GC41328D

A batch of the protic ionic liquid pyrrolidinium nitrate exploded while drying it under reduced pressure at 110 °C, using a rotary evaporator with an oil bath.



Structure of the protic ionic liquid pyrrolidinium nitrate.

(24) Sunlight, electrochemistry, and sustainable oxidation reactions

Green Chem., 2013, Advance Article
DOI: 10.1039/C3GC41650J

Inexpensive, readily available photovoltaic cells have been used to conduct indirect electrochemical oxidation reactions. The reactions retain the efficiency of the solar-electrochemical method while capitalizing on the unique opportunities for selectivity afforded by a chemical oxidant. The versatility of the electrochemical method allowed for the recycling of Os(VIII)-, TEMPO-, Ce(IV)-, Pd(II)-, Ru(VIII)-, and Mn(V)-oxidants all with the same very simple reaction apparatus.

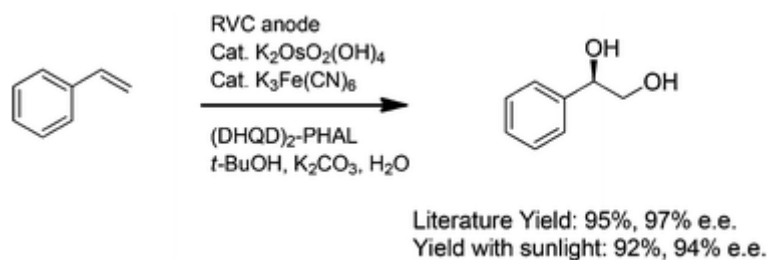




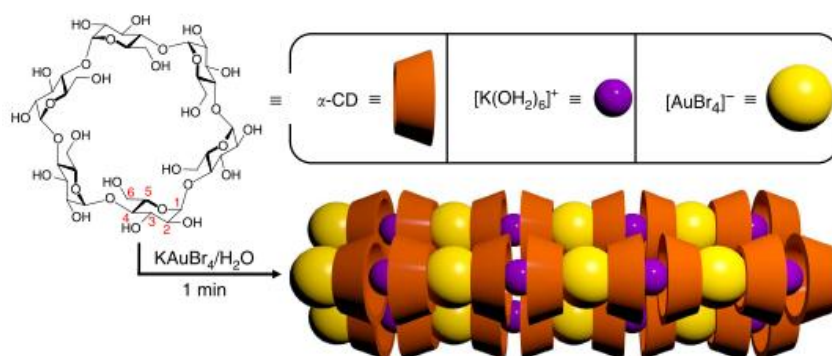
Fig. 1 An electrochemical reaction setup with a simple 6 V photovoltaic power supply is shown. The ammeter is spliced into the line so that the current passed through the flask can be monitored.

(25) Selective isolation of gold facilitated by second-sphere coordination with α -cyclodextrin (isolation of gold without using cyanide)

Nature Communications, 4:1855

DOI: 10.1038/ncomms2891

Gold recovery using environmentally benign chemistry is imperative from an environmental perspective. Here we report the spontaneous assembly of a one-dimensional supramolecular complex with an extended $\{[K(OH_2)_6][AuBr_4]C(\alpha\text{-cyclodextrin})_2\}_n$ chain superstructure formed during the rapid co-precipitation of α -cyclodextrin and $KAuBr_4$ in water. This phase change is selective for this gold salt, even in the presence of other square-planar palladium and platinum complexes. From single-crystal X-ray analyses of six inclusion complexes between α -, β - and γ -cyclodextrins with $KAuBr_4$ and $KAuCl_4$, we hypothesize that a perfect match in molecular recognition between α -cyclodextrin and $[AuBr_4]^-$ leads to a near-axial orientation of the ion with respect to the α -cyclodextrin channel, which facilitates a highly specific second-sphere coordination involving $[AuBr_4]^-$ and $[K(OH_2)_6]^+$ and drives the co-precipitation of the 1:2 adduct. This discovery heralds a green host-guest procedure for gold recovery from gold-bearing raw materials making use of α -cyclodextrin—an inexpensive and environmentally benign carbohydrate.

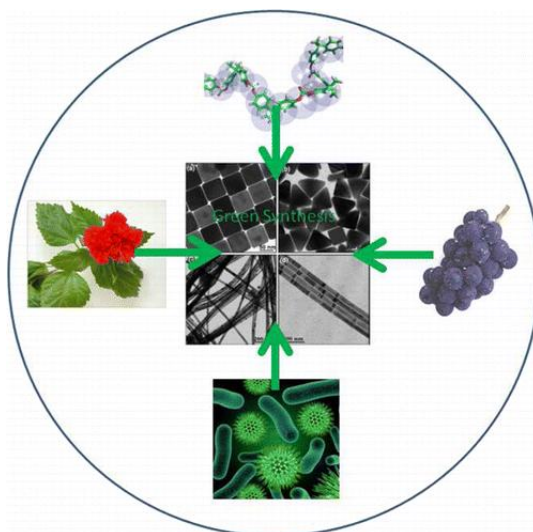


(26) Greener Techniques for the Synthesis of Silver Nanoparticles Using Plant Extracts, Enzymes, Bacteria, Biodegradable Polymers, and Microwaves

ACS Sustainable Chem. Eng., 2013, 1 (7), pp 703 – 712

DOI: 10.1021/sc4000362

The use of silver nanoparticles (AgNPs) is gaining in popularity due to silver's antibacterial properties. Conventional methods for AgNP synthesis require dangerous chemicals and large quantities of energy (heat) and can result in formation of hazardous byproducts. This article summarizes recent activity in this general area where environmentally friendly synthetic techniques are currently being explored for the synthesis of "greener" AgNPs including the use of plant extracts, biodegradable polymers, and enzymes/bacteria and alternative energy input systems, such as microwave irradiation. Microwave heating enables efficient formation of nanostructures of uniform small sizes in shorter reaction times with reduced energy consumption; preventing agglomeration of ensuing nanoparticles is an additional attribute.



(27) Recalcitrance of Nature: Chemocatalysis for the Production of Biomass-Based Building Blocks (editorial), read the related articles in this special issue.

ChemSusChem, Volume 6, Issue 9, pages 1559 – 1563, 2013

DOI:10.1002/cssc.201300602

Catch me if you can: Since its early days catalysis science and technology has shaped our society and provided us with the means and goods to enjoy a more prosperous life.

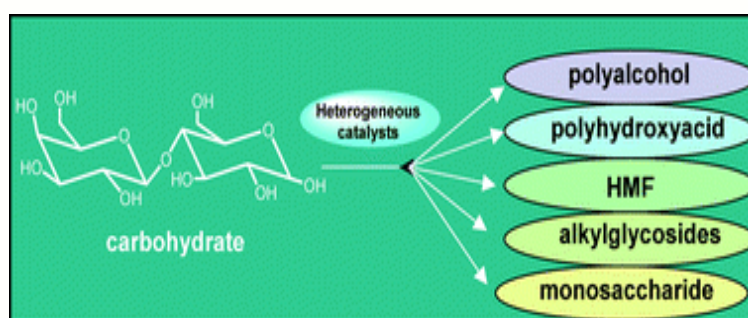
Chemocatalytic conversion is a key enabler for the efficient utilization of biomass, an important factor in this new era of sustainability. This Special Issue of *ChemSusChem* is dedicated to state-of-the-art chemistry within the field, specifically focusing on the joint research efforts in The Netherlands within the public – private research consortium CatchBio.



(28) Converting carbohydrates to bulk chemicals and fine chemicals over heterogeneous catalysts

Green Chem., 2011,13, 520-540.
DOI:10.1039/C0GC00639D

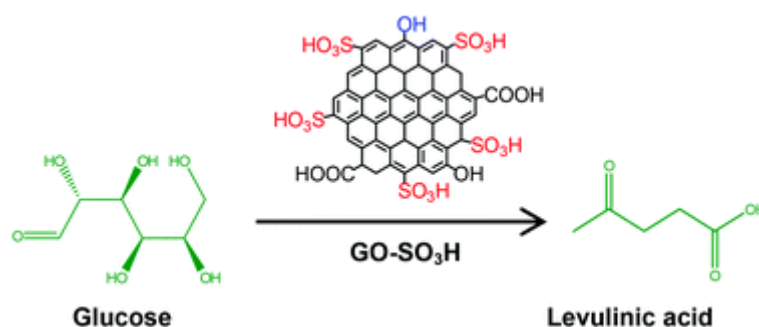
In this Critical Review, we discuss how carbohydrates can be transformed into a variety of chemicals through heterogeneous catalysis. We focus particularly on oxidation, reduction and dehydration of hexoses, as well as one-pot reactions of di- and polysaccharides. Most of the reactions involve heterogeneous catalysts, although some interesting homogeneously catalyzed processes are also included.



(29) Chemical conversion of biomass-derived hexose sugars to levulinic acid over sulfonic acid-functionalized graphene oxide catalysts

Green Chem., 2013,15, 2935-2943
DOI: 10.1039/C3GC40353J

Heterogeneous graphene oxide (GO)-based catalysts with sulfonic acid (SO₃H) functional groups (GO – SO₃H) were used for the selective decomposition of the hexose sugars, glucose and fructose into levulinic acid (LA), which has been used as a platform chemical for various value-added derivatives. The GO – SO₃H catalysts gave high yields of around 78% for LA and showed good reuse compatibility with reliable performance. The chemical transformation patterns for hexose sugar decompositions are affected by the temperature, the density of acid sites, and the type of catalyst. The high catalytic performance of GO – SO₃H was shown to result from the higher density of Brønsted acid sites in the GO, compared with the Lewis acid sites in other AC – SO₃H catalysts. The morphology, surface characteristics, and other physiochemical properties were evaluated using several characterization techniques.

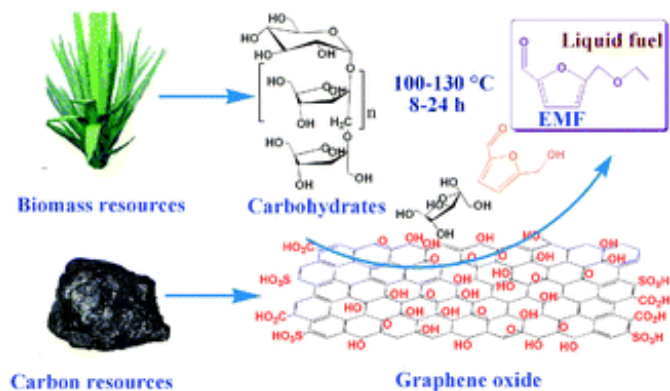


(30) Graphene oxide as a facile acid catalyst for the one-pot conversion of carbohydrates into 5-ethoxymethylfurfural

Green Chem., 2013,15, 2379-2383

DOI:10.1039/C3GC41109E

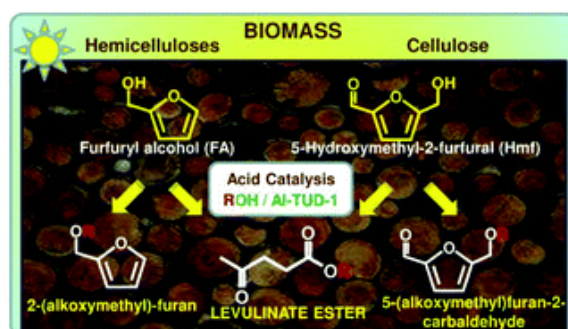
Graphene oxide obtained by the Hummers method was discovered to be an efficient and recyclable acid catalyst for the conversion of fructose-based biopolymers into 5-ethoxymethylfurfural (EMF). EMF yields of 92%, 71%, 34% and 66% were achieved when 5-hydroxymethylfurfural (HMF), fructose, sucrose and inulin were used as starting materials, respectively.



(31) Production of biomass-derived furanic ethers and levulinate esters using heterogeneous acid catalysts

Green Chem., 2013, Advance Article
DOI:10.1039/C3GC41908H

Mesoporous aluminosilicates of the type Al-TUD-1, prepared *via* “green”, low-cost, non-surfactant templating routes, are effective and versatile heterogeneous acid catalysts for the production of useful bio-based furanic ethers and levulinate esters, *via* the reactions of the biorenewable substrates 5-hydroxymethyl-2-furfural (Hmf) or furfuryl alcohol (FA) with aliphatic alcohols. The identification of reaction intermediates and products by comprehensive two-dimensional gas chromatography combined with time-of-flight mass spectrometry was carried out, giving mechanistic insights. Ethyl levulinate (EL) was formed from FA or Hmf as substrates, with higher EL yields being reached in the former case. Different types of alkyl levulinates may be synthesized from FA using Al-TUD-1 catalysts. On the other hand, 5-(ethoxymethyl)furan-2-carbaldehyde may be formed as the main product from Hmf. Modifications of the properties of Al-TUD-1 involved varying the Si/Al ratio and applying a post-synthesis acid treatment. The influence of these factors and of the reaction conditions on the catalytic reactions was investigated. The efficient regeneration and recyclability of Al-TUD-1 was assessed.

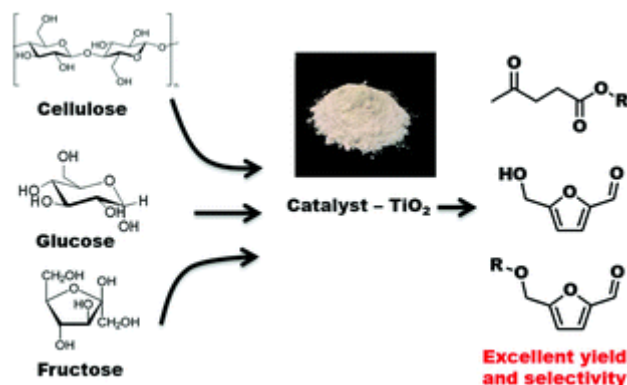


(32) Heterogeneous acidic TiO₂ nanoparticles for efficient conversion of biomass derived carbohydrates

Green Chem., 2013, Advance Article

DOI:10.1039/C3GC40909K

Selective conversion of biomass derived carbohydrates into fine chemicals is of great significance for the replacement of petroleum feedstocks and the reduction of environmental impacts. Levulinic acid, 5-hydroxymethyl furfural (HMF) and their derivatives are recognized as important precursor candidates in a variety of different areas. In this study, the synthesis, characterization, and catalytic activity of acidic TiO₂ nanoparticles in the conversion of biomass derived carbohydrates were explored. This catalyst was found to be highly effective for selective conversion to value-added products. The nanoparticles exhibited superior activity and selectivity towards methyl levulinate from fructose in comparison to current commercial catalysts. The conversion of fructose to methyl levulinate was achieved with 80% yield and high selectivity (up to 80%). Additionally, conversions of disaccharides and polysaccharides were studied. Further, the production of versatile valuable products such as levulinic esters, HMF, and HMF-derived ethers was demonstrated using the TiO₂ nano-sized catalysts in different solvent systems.



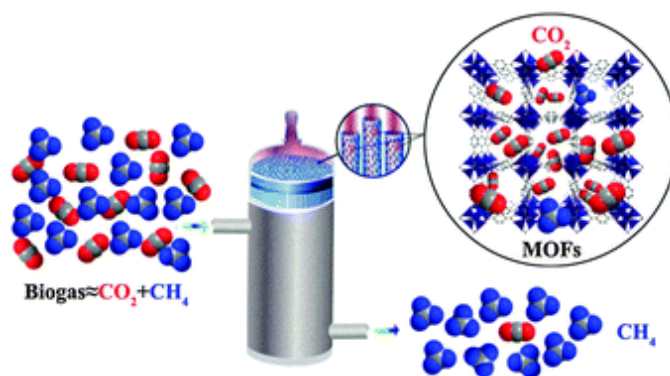
(33) Metal - organic frameworks for upgrading biogas *via* CO₂ adsorption to biogas green energy

Chem. Soc. Rev., 2013, Advance Article

DOI: 10.1039/C3CS60244C

In the midst of the global climate change phenomenon, mainly caused by fossil fuel burning to provide energy for our daily life and discharge of CO₂ into the atmosphere,

biogas is one of the important renewable energy sources that can be upgraded and applied as a fuel source for energy in daily life. The advantages of the production of hybrid materials, metal – organic framework (MOF) adsorbents, expected for the biogas upgrading, rely on the bulk separation of CO₂ under near-ambient conditions. This review highlights the challenges for MOF adsorbents, which have the greatest upgrading abilities for biogas *via* **selective passage of methane**. The key factors improving the ideal MOF materials for these high CO₂ capture and selectivity uses for biogas upgrading to produce bio-methane and reduce fossil-fuel CO₂ emission will be discussed.



V. A Few Papers on Methane Activation

(34) Efficient oxidation of methane to methanol by dioxygen mediated by tricopper clusters

Angewandte Chemie - International Edition, Volume 52, Issue 13, 25 March 2013, Pages 3731-3735

TONs of copper fun: There is considerable interest in developing catalysts to harness the abundant natural supply of methane for various industrial applications. Two tricopper complexes capable of mediating efficient oxidation of methane to methanol under ambient conditions were tested: a biomimetic tricopper complex (see figure) and a tricopper-peptide species derived from the particulate methane monooxygenase (pMMO) protein

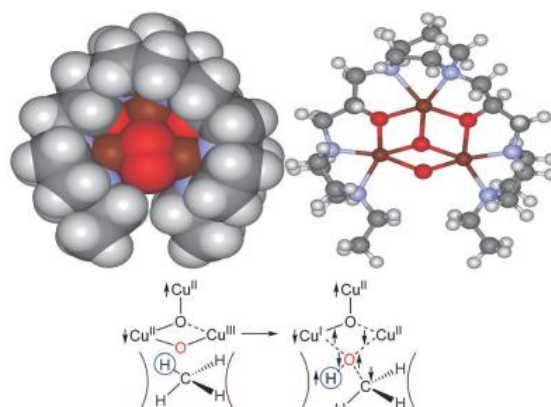


Figure 3. Space-filling model (left) and ball-and-stick model (right) of the optimized structure of $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(\mu\text{-O})_2\text{Cu}^{\text{II}}(7\text{-N-Etppz})]^+$ showing the funnel-like opening or cleft at the bottom for a hydrocarbon substrate to access the "hot" oxene group. H white, C gray, N blue, O red, Cu brown. Formation of the transition-state complex during facile singlet oxene transfer to methane from a dioxygen-activated tricopper complex is shown at the bottom.

(35) Efficient room-temperature oxidation of hydrocarbons mediated by tricopper cluster complexes with different ligands

Advanced Synthesis and Catalysis, Volume 354, Issue 17, 26 November 2012, Pages 3275-3282

Six tricopper cluster complexes of the type $[\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}(\text{L})]^+$ supported by a series of multidentate ligands (L) have been developed as oxidation catalysts. These complexes are capable of mediating the facile oxygen-atom transfer to hydrocarbon substrates like cyclohexane, benzene, and styrene (C_6H_{12} , C_6H_6 and C_8H_8) upon activation by hydrogen peroxide at room temperature. The processes are catalytic with high turnover frequencies (TOF), efficiently oxidizing the substrates to their corresponding alcohols, aldehydes, and ketones in moderate to high yields. The catalysts are robust with turnover numbers (TON) limited only by the availability of hydrogen peroxide used to drive the catalytic turnover. The TON is independent of the substrate concentration and the TOF depends linearly on the hydrogen peroxide concentration when the oxidation of the substrate mediated by the activated tricopper complex is rapid. At low substrate concentrations, the catalytic system exhibits abortive cycling resulting from competing reduction of the activated catalyst by hydrogen peroxide. This behaviour of the system is consistent with activation of the tricopper complex by hydrogen peroxide to generate a strong oxidizing intermediate capable of a facile direct "oxygen-atom" transfer to the substrate upon formation of a transient complex between the activated catalyst and the substrate. Some substrate specificity has also been noted by varying the ligand design. These properties of the

tricopper catalyst are characteristic of many enzyme systems, such as cytochrome P450, which participate in biological oxidations.

(36) Designing Catalysts for Functionalization of Unactivated C – H Bonds Based on the CH Activation Reaction

Acc. Chem. Res., 2012, 45 (6), pp 885 – 898

DOI: 10.1021/ar200250r

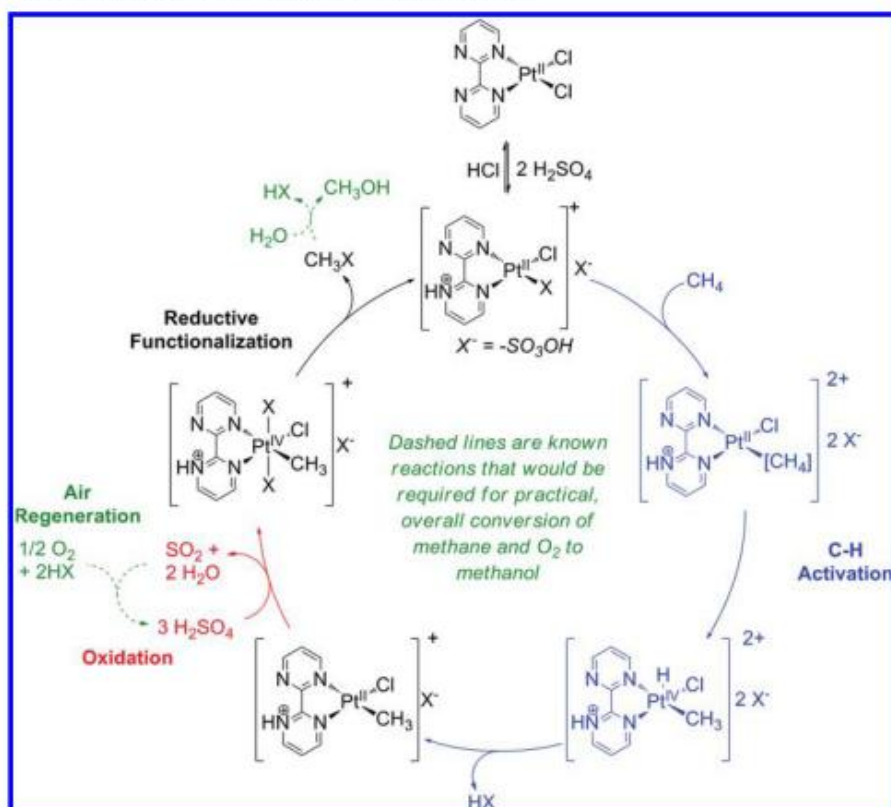
In an effort to augment or displace petroleum as a source of liquid fuels and chemicals, researchers are seeking lower cost technologies that convert natural gas (largely methane) to products such as methanol. Current methane to methanol technologies based on highly optimized, indirect, high-temperature chemistry (>800 °C) are prohibitively expensive. A new generation of catalysts is needed to rapidly convert methane and O₂ (ideally as air) directly to methanol (or other liquid hydrocarbons) at lower temperatures (~250 °C) and with high selectivity.

Our approach is based on the reaction between CH bonds of hydrocarbons (RH) and transition metal complexes, L_nM-X, to generate activated L_nM-R intermediates while avoiding the formation of free radicals or carbocations. We have focused on the incorporation of this reaction into catalytic cycles by integrating the activation of the CH bond with the functionalization of L_nM-R to generate the desired product and regenerate the L_nM-X complex. To avoid free-radical reactions possible with the direct use of O₂, our approach is based on the use of air-recyclable oxidants. In addition, the solvent serves several roles including protection of the product, generation of highly active catalysts, and in some cases, as the air-regenerable oxidant.

We postulate that there could be three distinct classes of catalyst/oxidant/solvent systems. The established electrophilic class combines electron-poor catalysts in acidic solvents that conceptually react by net removal of electrons from the bonding orbitals of the CH bond. The solvent protects the CH₃OH by conversion to more electron-poor [CH₃OH₂]⁺ or the ester and also increases the electrophilicity of the catalyst by ligand protonation. The nucleophilic class matches electron-rich catalysts with basic solvents and conceptually reacts by net donation of electrons to the antibonding orbitals of the CH bond. In this case, the solvent could protect the CH₃OH by deprotonation to the more electron-rich [CH₃O]⁻ and increases the nucleophilicity of the catalysts by ligand deprotonation. The third grouping involves ambiphilic catalysts that can conceptually

react with both the HOMO and LUMO of the CH bond and would typically involve neutral reaction solvents. We call this continuum base- or acid-modulated (BAM) catalysis. In this Account, we describe our efforts to design catalysts following these general principles. We have had the most success with designing electrophilic systems, but unfortunately, the essential role of the acidic solvent also led to catalyst inhibition by CH_3OH above ~ 1 M. The amphiphilic catalysts reduced this product inhibition but were too slow and inefficient. To date, we have designed new base-assisted CH activation and L_M -R functionalization reactions and are working to integrate these into a complete, working catalytic cycle. Although we have yet to design a system that could supplant commercial processes, continued exploration of the BAM catalysis continuum may lead to new systems that will succeed in addressing this valuable goal.

SCHEME 3. Proposed Mechanism for the "Periana System" for Methane Oxidation

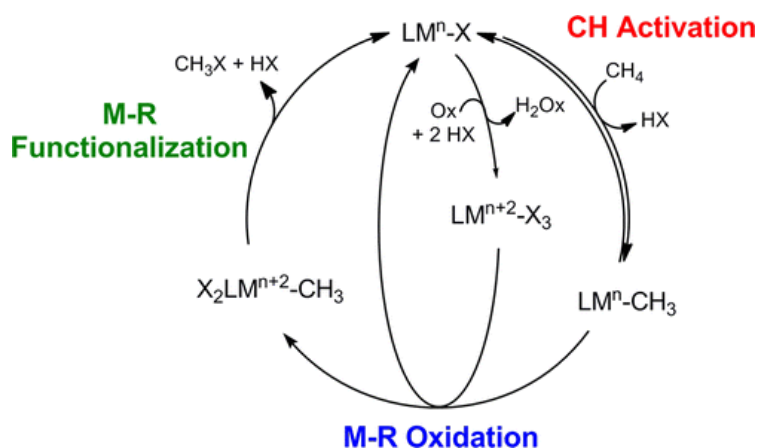


(37) Using Reduced Catalysts for Oxidation Reactions: Mechanistic Studies of the "Periana-Catalytica" System for CH_4 Oxidation

J. Am. Chem. Soc., 2013, 135 (39), pp 14644 – 14658

DOI: 10.1021/ja404895z

Designing oxidation catalysts based on CH activation with reduced, low oxidation state species is a seeming dilemma given the proclivity for catalyst deactivation by overoxidation. This dilemma has been recognized in the Shilov system where reduced Pt^{II} is used to catalyze methane functionalization. Thus, it is generally accepted that key to replacing Pt^{IV} in that system with more practical oxidants is ensuring that the oxidant does not over-oxidize the reduced Pt^{II} species. The “Periana-Catalytica” system, which utilizes $(\text{bpym})\text{Pt}^{\text{II}}\text{Cl}_2$ in concentrated sulfuric acid solvent at 200 °C, is a highly stable catalyst for the selective, high yield oxy-functionalization of methane. In lieu of the over-oxidation dilemma, the high stability and observed rapid oxidation of $(\text{bpym})\text{Pt}^{\text{II}}\text{Cl}_2$ to Pt^{IV} in the absence of methane would seem to contradict the originally proposed mechanism involving CH activation by a reduced Pt^{II} species. Mechanistic studies show that the originally proposed mechanism is incomplete and that while CH activation does proceed with Pt^{II} there is a solution to the over-oxidation dilemma. Importantly, contrary to the accepted view to minimize Pt^{II} overoxidation, these studies also show that increasing that rate could increase the rate of catalysis and catalyst stability. The mechanistic basis for this counterintuitive prediction could help to guide the design of new catalysts for alkane oxidation that operate by CH activation.



(38) C - H Functionalization special issue (editorial) . refer to the related articles in this special issue.

Acc. Chem. Res., 2012, 45 (6), pp 777 - 777

DOI: 10.1021/ar300096z

C–H Functionalization

The conversion of a C–H bond to a C–Z bond where Z is an atom other than hydrogen is the most encompassing transformation in organic chemistry. Yet it has also proven to be one of the most challenging for synthetic chemists to accomplish selectively in the laboratory. In nature, this transformation is essential for metabolism, and individual enzymes have evolved to carry out very specific conversions. In industry, the C–H to C–Z conversion is a core component in energy, fine chemical, and pharmaceutical production, but often the methods used to carry out these conversions involve multiple steps, generate significant byproducts, and/or are energy intensive. Direct transformations of C–H bonds have long been known from reactions in organic chemistry as unselective oxidation processes. However, more recent efforts by investigators around the world have produced refinements that offer high selectivity, and it is for these processes that the term “C–H functionalization” is currently used.

The C–H bond has been called the “unfunctional” group. It is highly stable and generally resistant to reactions with acids and bases or electrophiles and nucleophiles. Early efforts in the area of C–H functionalization have been successful in using functional groups that are attached to carbon to change the reactivity of the nearby C–H bond and contribute to its cleavage. In contrast, more recent efforts have sought to perform transformations on C–H bonds that are not activated by adjacent functional groups: selective C–H functionalization of unactivated C–H bonds. Selective transformations of C–H bonds are even more challenging in complex molecules that have multiple C–H bonds that are electronically similar. Thus, selectivity includes not only chemoselectivity but also regioselectivity and stereoselectivity.

The pathway to activation and cleavage of the C–H bond is central to understanding how selectivity can be achieved. In its early incarnation, the C–H to C–Z bond conversion was focused on free radical oxidative processes or carbene insertion reactions that, for the most part, were unselective. Advances in organometallic chemistry have

informed us on how reactivity and selectivity in reactions with C–H bonds could be modified to achieve high selectivity, and the outcome of these advances is revealed in the Accounts that are included in this Special Issue. However, the C–H bond cleavage is only one aspect of functionalization. To achieve high selectivity, understanding of both the path for formation of the new C–Z bond, and of how the catalyst can be recycled, is also needed.

This Special Issue of Accounts covers the breadth of C–H functionalizations that extends from the transformation of alkanes to the synthesis of complex molecules. New advances in method development are revealed. Strategies and successes in selective C–H bond activation and cleavage are presented along with functionalization by dehydrogenation, insertions, or oxidations. Metal carbene chemistry is the basis for recent developments in highly regio- and stereoselective carbenoid insertion reactions. Oxidative transformations that offer directed C–H functionalization and utilization of dioxygen extend the dimensions of C–H functionalization. We are grateful to our esteemed colleagues who have contributed to this issue. They have filled the pages that follow with their unique stories describing their remarkable strategies and achievements in catalysis, mechanistic investigations, synthetic methodologies, and applications, all directed to realizing selective functionalization of the “unfunctional” C–H bond.

Michael P. Doyle
University of Maryland

Karen I. Goldberg
University of Washington
Guest Editors

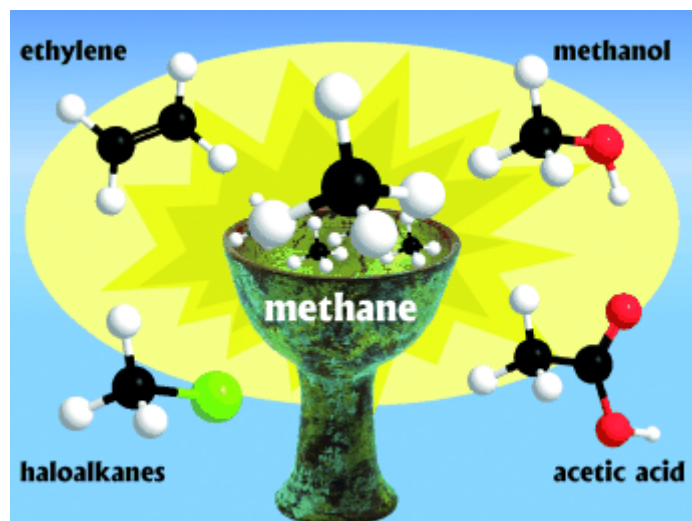
(39) Oxidative methane upgrading

ChemSusChem, Volume 5, Issue 9, September 2012, Pages 1668-1686

DOI:10.1002/cssc.201200299

The economically viable oxidative upgrading of methane presents one of the most difficult but rewarding challenges within catalysis research. Its potential to revolutionise the

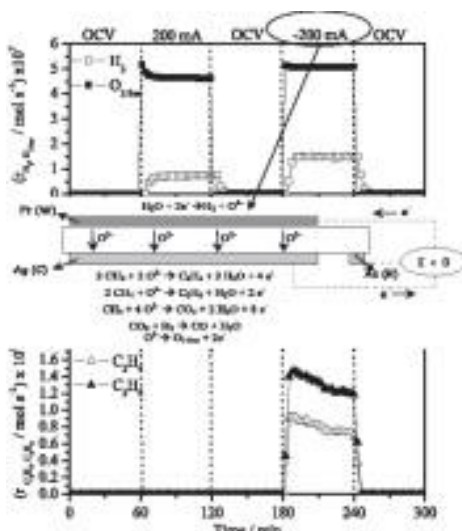
chemical value chain, coupled with the associated supremely challenging scientific aspects, has ensured this topic's high popularity over the preceding decades. Herein, we report a non-exhaustive account of the current developments within the field of oxidative methane upgrading and summarise the pertaining challenges that have yet to be solved.



(40) [Simultaneous production of H₂ and C₂ hydrocarbons by gas phase electrocatalysis](#)

Applied Catalysis B: Environmental, 113-114 (2012) 192-200

This study reports, for the first time in literature, the possibility of simultaneously producing H₂ and C_{2s} hydrocarbons by using an anionic single chamber solid electrolyte cell of Pt/YSZ/Ag (working/solid electrolyte/counter) tested under a humidified CH₄ atmosphere (no direct O₂ feeding gas to the reactor). Hydrogen was mainly produced in the Pt working electrode under application of negative polarizations by a steam electrolysis process ($\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + \text{O}^{2-}$). Simultaneously, the produced O²⁻ ions were electrochemically pumped to the Ag counter electrode, leading to the production of C_{2s} hydrocarbons (ethane and ethylene), via oxidative coupling of CH₄ ($\text{CH}_4 + \text{O}^{2-} \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 + 2\text{e}^-$). The influence of the applied current, reaction temperature and feeding composition on the electrocatalytic performance of the cell was evaluated for both processes. It was found that the possibility of controlling the rate of O²⁻ supply allows to control and optimize the production rate of the desired compounds (H₂ and C_{2s}) at varying the reaction conditions. In addition, the stability of the cell for long polarization times has been demonstrated under the optimal conditions for the production of both compounds.

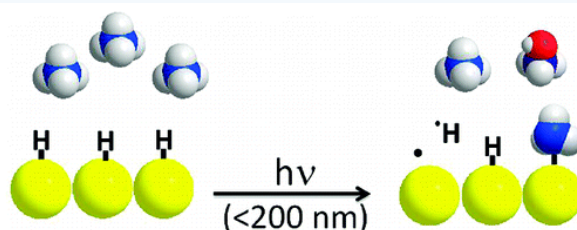


(41) Selective, Room-Temperature Transformation of Methane to C1 Oxygenates by Deep UV Photolysis over Zeolites

J. Am. Chem. Soc., 2011, 133 (43), pp 17257 – 17261

DOI: 10.1021/ja204559z

Methane can directly be transformed into liquid C₁ oxygenated products with selectivities above 95% at 13% conversion by deep UV photocatalysis, in the presence of H₂O and air. Pure silica zeolites, and more specifically, beta zeolite with a large number of internal silanol groups is active and selective, while amorphous silica with no micropores is much less efficient. Irradiation produces the homolytic cleavage of surface hydroxyl groups, leading to silyloxyl radicals that will generate methyl radicals from methane. The selectivity arises from the occurrence of the reaction in a confined space restricting the mobility of the radical intermediates that will be mostly attached to the solid surface. Energy consumption of the process is in the order of 7.2 Gcal × mol⁻¹ that compares very favorably with the energy required for transforming methane to synthesis gas (15.96 Gcal × mol⁻¹).



(42) Conversion of Methane into C1 Oxygenates by Deep-UV Photolysis on Solid Surfaces: Influence of the Nature of the Solid and Optimization of Photolysis Conditions

Chemistry – European Journal, 2012, 18 (6), 1820-1825.A

DOI: 10.1002/chem.201102273

Deep-UV photolysis (either 165 or 185 nm) of surface hydroxy groups leads to homolytic O—H bond-cleavage with the generation of oxyl radicals that can initiate the room-temperature radical-chain methane activation. Whilst in the absence of oxygen, radical coupling reactions to give low-molecular-weight alkanes are observed in the gas phase, the presence of some oxygen quenches these radicals and increases the selectivity towards C1 oxygenates (methanol, formaldehyde, and formic acid species). The nature of the solid influences the efficiency of the photochemical process and the distribution between products in the gas and solid phases. Using Beta-, delaminated ITQ2 and ITQ6, and medium-pore ZSM5 zeolites, mesoporous MCM41 silicates, and non-porous TiO₂, we observed that confinement and porosity increased the proportion of C1 oxygenates adsorbed onto the solid and reduced the contribution of the gas-phase products. In addition, the presence of aluminum in the zeolite framework, which is responsible for the generation of acid sites, increased overoxidation of methanol and methoxy groups into formaldehyde and formic acids. For a given amount of methane and unchanged photolysis conditions, the conversion increased with the amount of the solid used as photocatalyst. In this way, methane conversions of up to 7 % were achieved for the 185 nm photolysis of methane for 1 h with a 76 MJ mol⁻¹ energy consumption.

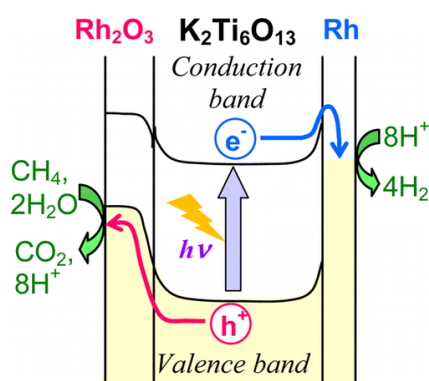
(43) Bifunctional Rhodium Cocatalysts for Photocatalytic Steam Reforming of Methane over Alkaline Titanate

ACS Catal., 2012, 2(10), pp 2126 – 2134

DOI: 10.1021/cs2006229

Photocatalytic steam reforming of methane (PSRM; $2 \text{ H}_2\text{O (g)} + \text{CH}_4 \rightarrow 4 \text{ H}_2 + \text{CO}_2$) was examined over metal-loaded K₂Ti₆O₁₃ photocatalysts. Although the production rate was improved by loading Pt cocatalyst on the K₂Ti₆O₁₃ photocatalyst, unfavorable formation of CO and gradual deactivation of photocatalyst were observed. On the other hand, a Rh-loaded K₂Ti₆O₁₃ sample showed two times higher activity than the Pt-loaded one did, and promoted the PSRM selectively without deactivation for many hours. In the highly

active Rh-loaded photocatalyst, the Rh cocatalyst existed as a mixture of small metallic rhodium and large rhodium oxide particles. The photocatalytic activity tests for hydrogen evolution and oxygen evolution from each aqueous solution of sacrificial reagent (methanol and silver nitrate, respectively) revealed that the metallic rhodium particles and the rhodium oxide particles could function as cocatalysts preferably for reduction and oxidation, respectively. Also on a $\text{Na}_2\text{Ti}_6\text{O}_{13}$ photocatalyst, a mixture of rhodium metal and oxide similarly enhanced the photocatalytic activity. Thus, it is suggested that the Rh cocatalyst on these alkaline titanates bifunctionally promoted the PSRM.



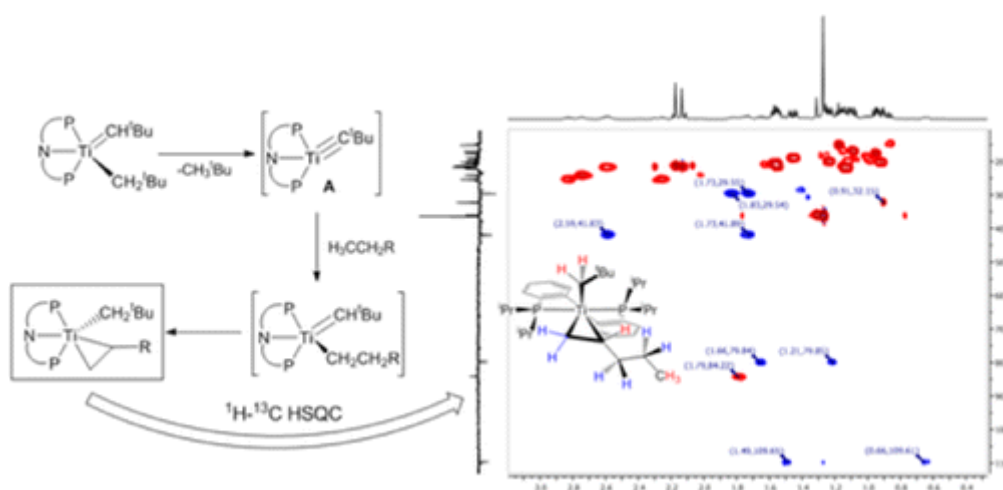
(44) [Room Temperature Dehydrogenation of Ethane, Propane, Linear Alkanes C4 – C8, and Some Cyclic Alkanes by Titanium – Carbon Multiple Bonds](#)

Journal of the American Chemical Society, 2013 135 (39), 14754-14767

DOI: 10.1021/ja4060178

The transient titanium neopentylidyne, $[(\text{PNP})\text{Ti}\equiv\text{C}^t\text{Bu}]$ (**A**; $\text{PNP}^- \equiv \text{N}[2\text{-P}^i\text{Pr}_2\text{-4-methylphenyl}]_2^-$), dehydrogenates ethane to ethylene at room temperature over 24 h, by sequential 1,2-CH bond addition and β -hydrogen abstraction to afford $[(\text{PNP})\text{Ti}(\eta^2\text{-H}_2\text{C}=\text{CH}_2)(\text{CH}_2^t\text{Bu})]$ (**1**). Intermediate **A** can also dehydrogenate propane to propene, albeit not cleanly, as well as linear and volatile alkanes C₄ – C₆ to form isolable α -olefin complexes of the type, $[(\text{PNP})\text{Ti}(\eta^2\text{-H}_2\text{C}=\text{CHR})(\text{CH}_2^t\text{Bu})]$ (R = CH₃ (**2**), CH₂CH₃ (**3**), ^{*n*}Pr (**4**), and ^{*n*}Bu (**5**)). Complexes **1** – **5** can be independently prepared from $[(\text{PNP})\text{Ti}=\text{CH}^t\text{Bu}(\text{OTf})]$ and the corresponding alkylating reagents, LiCH₂CHR (R = H, CH₃(unstable), CH₂CH₃, ^{*n*}Pr, and ^{*n*}Bu). Olefin complexes **1** and **3** – **5** have all been characterized by a diverse array of multinuclear NMR spectroscopic experiments including ¹H – ³¹P HOESY, and in the case of the α -olefin adducts **2** – **5**, formation of mixtures of two diastereomers (each with their corresponding pair of enantiomers) has been unequivocally established. The latter has been spectroscopically elucidated by NMR via C – H coupled and decoupled ¹H – ¹³C multiplicity edited gHSQC, ¹H – ³¹P HMBC, and

dqfCOSY experiments. Heavier linear alkanes (C_7 and C_8) are also dehydrogenated by **A** to form $[(PNP)Ti(\eta^2-H_2C=CH^nPentyl)(CH_2^tBu)]$ (6) and $[(PNP)Ti(\eta^2-H_2C=CH^pHexyl)(CH_2^tBu)]$ (7), respectively, but these species are unstable but can exchange with ethylene (1 atm) to form **1** and the free α -olefin. Complex **1** exchanges with $D_2C=CD_2$ with concomitant release of $H_2C=CH_2$. In addition, deuterium incorporation is observed in the neopentyl ligand as a result of this process. Cyclohexane and methylcyclohexane can be also dehydrogenated by transient **A**, and in the case of cyclohexane, ethylene (1 atm) can trap the $[(PNP)Ti(CH_2^tBu)]$ fragment to form **1**. Dehydrogenation of the alkane is not rate-determining since pentane and pentane- d_2 can be dehydrogenated to **4** and **4- d_2** with comparable rates (KIE = 1.1(0) at ~ 29 °C). Computational studies have been applied to understand the formation and bonding pattern of the olefin complexes. Steric repulsion was shown to play an important role in determining the relative stability of several olefin adducts and their conformers. The olefin in **1** can be liberated by use of N_2O , organic azides (N_3R ; R = 1-adamantyl or $SiMe_3$), ketones ($O=CPh_2$; 2 equiv) and the diazoalkane, $N_2CHtolyl_2$. For complexes **3** – **7**, oxidation with N_2O also liberates the α -olefin.



(45) Visible-light mediated heterogeneous C – H functionalization: oxidative multi-component reactions using a recyclable titanium dioxide (TiO_2) catalyst

Green Chem., 2013,15, 2056-2059

DOI:10.1039/C3GC40587G

Visible-light mediated heterogeneous C – H functionalization of tertiary amines provides access to a variety of α -amino amides. An oxidative, titanium dioxide catalyzed, Ugi-type,

three-component reaction has been developed in which the catalyst can be recycled without loss of activity.

