Contents

VIP The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:

*J. Steill, J. Zhao, C.-K. Siu, Y. Ke, U. H. Verkerk, J. Oomens, R. C. Dunbar, A. C. Hopkinson, K. M. Siu**
Structure of the Observable Histidine Radical Cation in the Gas Phase: a Captodative α Radical Ion

C. Schäffer, A. Merca, H. Bögge, A. M. Todea, M. L. Kistler, T. Liu, R. Thouvenot, P. Gouzerh, A. Müller**
Unprecedented and Differently Applicable Pentagonal Units in a Dynamic Library: A Keplerate of the Type $\{(W)W_5\}_{12}\{Mo_2\}_{30}$

*S. W. Hong, M. Byun, Z. Lin**
Robust Self-Assembly of Highly Ordered Complex Structures by Controlled Evaporation of Confined Microfluids

L. Catala, D. Brinzei, Y. Prado, A. Gloter, O. Stéphan, G. Rogez, T. Mallah**
Core–Multishell Magnetic Coordination Nanoparticles: Towards Multifunctionality at the Nanoscale

*D. Morton, S. Leach, C. Cordier, S. Warriner, A. Nelson**
Synthesis of Natural-Product-Like Molecules with over Eighty Distinct Scaffolds

*P. Hazarika, S. M. Jickells, K. Wolff, D. A. Russell**
Imaging of Latent Fingerprints Through the Detection of Drugs and Metabolites

Obituary

Jay Kazuo Kochi (1927–2008)
R. Rathore ——— **9186**

Anniversary

The Catalysis Society of Japan (CATSJ) celebrates its 50th anniversary this year. A brief history, summary of its activities, and outlook is presented.

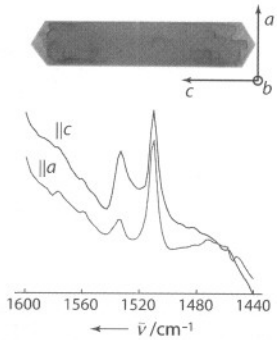
Catalysis Society of Japan

Y. Iwasawa,* M. Iwamoto, T. Deguchi, Y. Kubota, M. Machida, H. Yamashita ——— **9180–9185**

The Catalysis Society of Japan (CATSJ): History and Activities

Highlights

Dynamic duo: Combined spectroscopy and microscopy techniques now allow the nature of active sites on zeolite catalysts to be determined in detail. For example, synchrotron IR microscopy reveals the dimeric carbocation of 4-fluorostyrene in a single crystal of ZSM-5 (see picture).



Zeolite Catalysis

R. A. Schoonheydt* ——— **9188–9191**

Morphology of and Catalysis in Single Crystals of Zeolites

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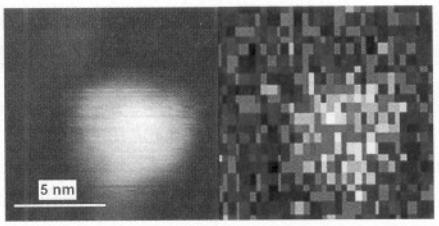
Contents

Minireviews

H_2O_2 Synthesis

J. K. Edwards, G. J. Hutchings* ——— **9192 – 9198**

Palladium and Gold–Palladium Catalysts for the Direct Synthesis of Hydrogen Peroxide



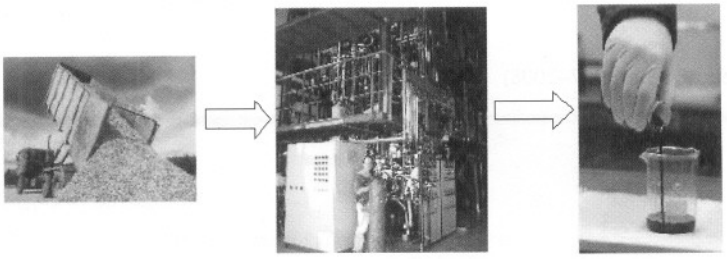
A great support act at the Palladium: In the search for an alternative to the current indirect industrial synthesis of H_2O_2, small nanoparticles of Au–Pd alloys have been shown to be highly active catalysts for the direct synthesis of H_2O_2 from O_2 and H_2. They do not require the addition of halide and phosphate stabilizers. The active particles comprise mainly Pd (blue, see picture) with some Au (green) supported on carbon (red).

Reviews

Renewable Resources

M. Stöcker* ——— **9200 – 9211**

Biofuels and Biomass-To-Liquid Fuels in the Biorefinery: Catalytic Conversion of Lignocellulosic Biomass using Porous Materials



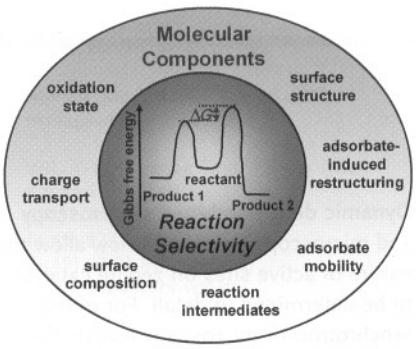
Wood, a renewable energy source, can be converted into fuels, chemicals, and energy products. An overview is presented of the processing of lignocellulose-rich starting materials into BTL (biomass-to-liquid) fuels, describes the complex reactions that take place at the porous catalysts in a biorefinery, and brings to light the challenges involved in the transition from pilot to production plants.

Catalyst Characteristics

G. A. Somorjai,* J. Y. Park — **9212 – 9228**

Molecular Factors of Catalytic Selectivity

The magnificent seven: The selectivity of heterogeneous catalyst processes has been defined on the molecular level by seven factors (see picture). These include the structure and the electronic properties of the surface, the type and mobility of the adsorbed species, as well as the charge transport and oxidation states of the catalyst.



For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Wiley-VCH, 111 River Street, Hoboken, NJ 07030. Annual subscription price for institutions: US$ 7225/6568 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

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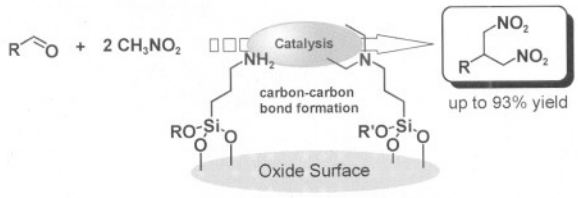
Communications

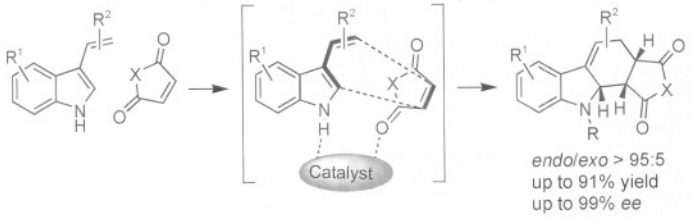


D'you know what amine? Primary and tertiary amines are both immobilized on the same silica–alumina surface by silane-coupling reactions. The resultant silica–alumina-supported double-amines are found to exhibit excellent catalysis for 1,3-dinitroalkane synthesis from various aldehydes with nitromethane. A cooperative catalytic mechanism on the solid surface for this efficient synthesis is proposed.

Heterogeneous Catalysis

K. Motokura, M. Tada, Y. Iwasawa* ——— **9230–9235**

Cooperative Catalysis of Primary and Tertiary Amines Immobilized on Oxide Surfaces for One-Pot C–C Bond Forming Reactions

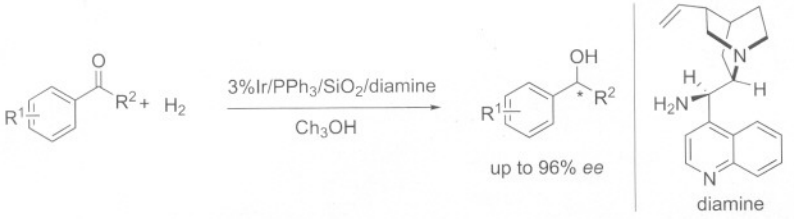


Diels or no Diels? A bifunctional organic catalyst based on the thiourea motif is able to coordinate both diene and dienophile in an unprecedented asymmetric Diels–Alder reaction of 3-vinylindole derivatives, giving a rapid access to optically active tetra- and hexahydrocarbazoles with excellent results in terms of yields, diastereoselectivities, and enantioselectivities.

Asymmetric Catalysis

C. Gioia, A. Hauville, L. Bernardi,* F. Fini, A. Ricci* ——— **9236–9239**

Organocatalytic Asymmetric Diels–Alder Reactions of 3-Vinylindoles



Catalyst support: The first highly enantioselective heterogeneous hydrogenation of aromatic ketones catalyzed by Ir/SiO_2 stabilized with Ph_3P and modified by a chiral diamine derived from a cinchona alkaloid is described (see scheme). The reaction can be employed for the reduction of a broad range of aromatic ketones to the corresponding alcohols with high enantioselectivity.

Heterogeneous Catalysis

H.-y. Jiang, C.-f. Yang, C. Li, H.-y. Fu, H. Chen,* R.-x. Li, X.-j. Li — **9240–9244**

Heterogeneous Enantioselective Hydrogenation of Aromatic Ketones Catalyzed by Cinchona- and Phosphine-Modified Iridium Catalysts

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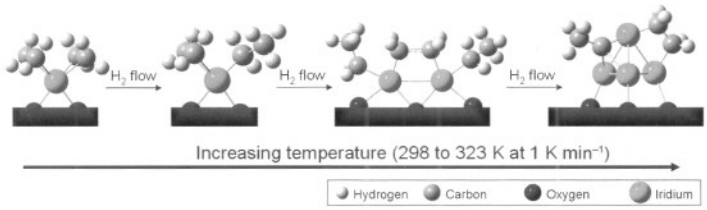
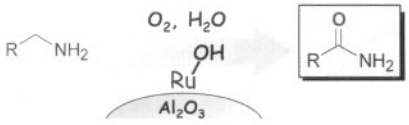


The chemistry of formation of iridium clusters from mononuclear iridium diethylene complexes anchored in dealuminated Y zeolite, and their subsequent breakup—all including changes in the metal–metal, metal–support, and metal–ligand interactions—is demonstrated by time-resolved EXAFS, XANES, and IR spectroscopy.

Cluster Formation

A. Uzun, B. C. Gates* ——— **9245 – 9248**

Real-Time Characterization of Formation and Breakup of Iridium Clusters in Highly Dealuminated Zeolite Y

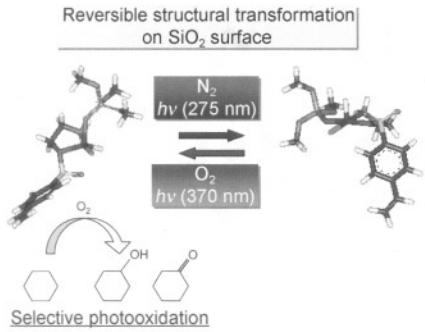


Supporting green chemistry: The supported ruthenium hydroxide $Ru(OH)_x/Al_2O_3$ acts as an efficient heterogeneous catalyst for the oxygenation of primary amines to primary amides (see scheme). Various primary amines (including aromatic, aliphatic, and heterocyclic) are converted in aqueous media, using air as the sole oxidant and producing only water as a by-product.

Amide Synthesis

J. W. Kim, K. Yamaguchi, N. Mizuno* ——— **9249 – 9251**

Heterogeneously Catalyzed Efficient Oxygenation of Primary Amines to Amides by a Supported Ruthenium Hydroxide Catalyst



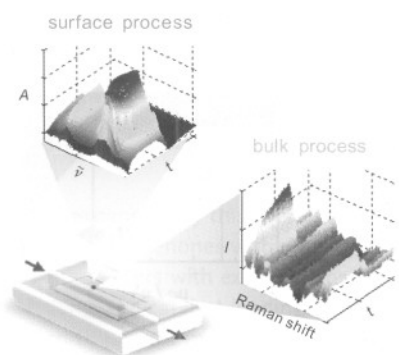
Ru experienced? Two novel coordinatively unsaturated SiO_2-supported Ru complexes were prepared by photoinduced ligand elimination, accompanied by dissociative coordination of a surface OH group to the unsaturated Ru center by photoirradiation. Wavelength- and atmosphere-dependent photoinduced reversible interconversion occurs between the two Ru complexes. One of the complexes is catalytically active for the photooxidation of cycloalkanes with O_2.

Heterogeneous Catalysis

M. Tada, Y. Akatsuka, Y. Yang, T. Sasaki, M. Kinoshita, K. Motokura, Y. Iwasawa* ——— **9252 – 9255**

Photoinduced Reversible Structural Transformation and Selective Oxidation Catalysis of Unsaturated Ruthenium Complexes Supported on SiO_2

What, where, when: A combination of both surface-sensitive (diffuse reflectance infrared Fourier transform spectroscopy, DRIFTS) and bulk-sensitive (Raman spectroscopy) detection at different catalyst-bed positions is shown to be a powerful tool to facilitate deeper understanding of complex dynamic surface and bulk processes, which occur widely in heterogeneous catalysis.



Heterogeneous Catalysis

A. Urakawa,* N. Maeda, A. Baiker ——— **9256 – 9259**

Space- and Time-Resolved Combined DRIFT and Raman Spectroscopy: Monitoring Dynamic Surface and Bulk Processes during NO_x Storage Reduction

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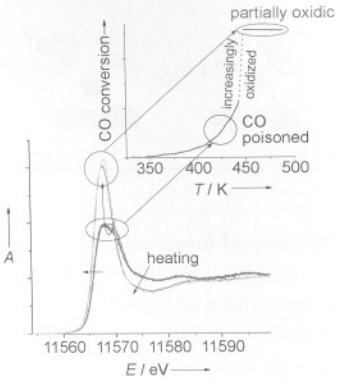
Contents

CO Oxidation

J. Singh, E. M. C. Alayon, M. Tromp, O. V. Safonova, P. Glatzel, M. Nachtegaal, R. Frahm, J. A. van Bokhoven* ——— **9260 – 9264**

Generating Highly Active Partially Oxidized Platinum during Oxidation of Carbon Monoxide over Pt/Al_2O_3: In Situ, Time-Resolved, and High-Energy-Resolution X-Ray Absorption Spectroscopy

High activity is generated by sudden formation of disordered oxidic platinum over a platinum catalyst supported on alumina (see picture). High temperature and low concentration of carbon monoxide are required to generate high activity.

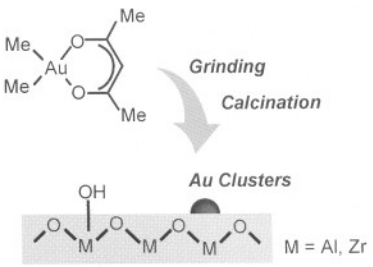


Gold Nanoparticles

T. Ishida, N. Kinoshita, H. Okatsu, T. Akita, T. Takei, M. Haruta* ——— **9265 – 9268**

Influence of the Support and the Size of Gold Clusters on Catalytic Activity for Glucose Oxidation

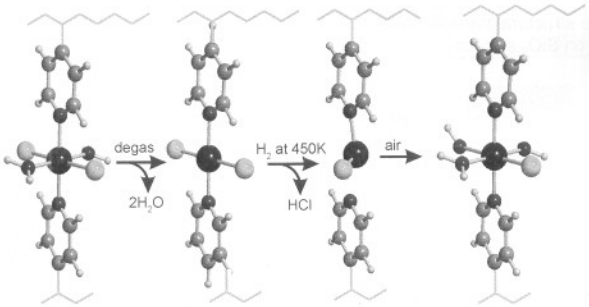
Not all that glitters... The activity of supported gold nanoparticles depends on the method used for their preparation. Gold clusters of about 2 nm in diameter were deposited on nonreducible metal oxides and carbon materials by solid grinding of a volatile organogold complex in a ball mill and subsequent calcination (see scheme). Au/ZrO_2 and Au/Al_2O_3 prepared in this way were extremely efficient catalysts for the aerobic oxidation of glucose.



Redox Chemistry

E. Groppo,* M. J. Uddin, S. Bordiga, A. Zecchina, C. Lamberti* — **9269 – 9273**

Structure and Redox Activity of Copper Sites Isolated in a Nanoporous P4VP Polymeric Matrix

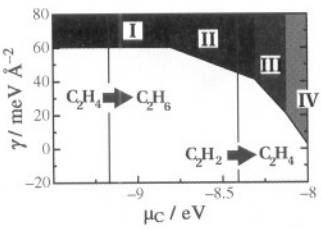


A flexible friend: The electronic and structural changes undergone by Cu sites grafted inside an amorphous nanoporous P4VP matrix during a simple redox process (representing more complex liquid-phase catalysis) were investigated by complementary in situ techniques (FTIR, UV/Vis, XAS spectroscopy) (see scheme; brown Cu, green Cl, blue N, red O). The flexibility of the polymeric structure was found to be the key factor in the reversibility of the redox process.

Heterogeneous Catalysis

D. Teschner,* Z. Révay, J. Borsodi, M. Hävecker, A. Knop-Gericke, R. Schlögl, D. Milroy, S. D. Jackson, D. Torres, P. Sautet ——— **9274 – 9278**

Understanding Palladium Hydrogenation Catalysts: When the Nature of the Reactive Molecule Controls the Nature of the Catalyst Active Phase



Alkynes of everything: Fundamental differences in the palladium-catalyzed hydrogenation of double and triple C—C bonds arise from marked differences in the composition of the catalyst surface. In situ X-ray photoelectron spectroscopy of the near-surface region of active palladium catalysts uncovers strong links between the chemical nature of the (alkyne/alkene) reactive molecules and the subsurface state of the catalyst (**I**–**IV**).

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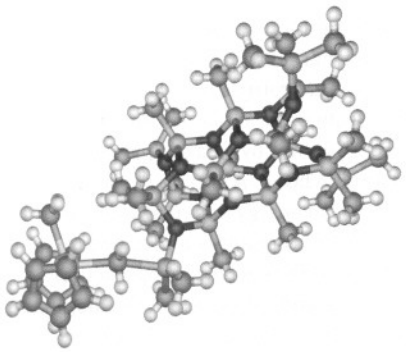


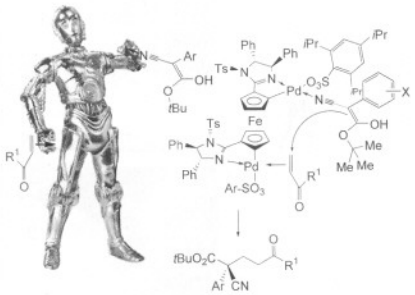
Tubular Al's: Quantum chemical calculations show the facile formation of nanotubular methylaluminoxanes from reactions between water and trimethylaluminum. The nanotubular methylaluminoxane is shown to be capable of activating metallocene catalysts for α-olefin polymerization (see structure; red O, bronze Al, blue Zr).

Polymerization Catalysis

M. Linnolahti,* J. R. Severn, T. A. Pakkanen _____ **9279 – 9283**

Formation of Nanotubular Methylaluminoxanes and the Nature of the Active Species in Single-Site α-Olefin Polymerization Catalysis

Robotlike: Low catalyst loadings of a planar-chiral ferrocenyl bispalladacycle are sufficient to catalyze the Michael addition of trisubstituted α-cyanoacetates to enones with excellent yields (TONs up to 2450) and high enantioselectivity. The reaction proceeds by a cooperative bimetallic mechanism and is superior to previous methods relying on soft Lewis acid catalysts.

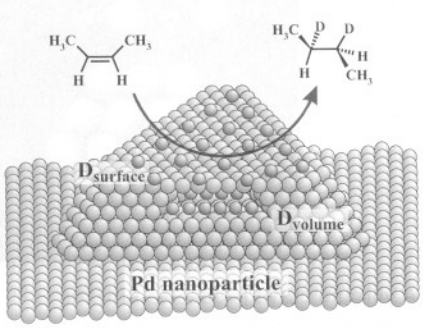


Bimetallic Catalysis

S. Jautze, R. Peters* _____ **9284 – 9288**

Enantioselective Bimetallic Catalysis of Michael Additions Forming Quaternary Stereocenters

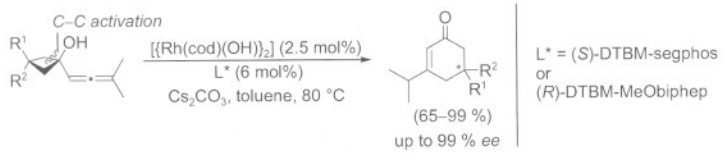
The mechanism of olefin hydrogenation on a supported noble-metal catalyst requires the presence of weakly bound hydrogen atoms absorbed in the volume of the metal particle (see picture). Co-adsorbed carbonaceous deposits affect the hydrogen distribution in the metal clusters and critically control their activity and selectivity in olefin conversions.



Heterogeneous Catalysis

M. Wilde,* K. Fukutani, W. Ludwig, B. Brandt, J.-H. Fischer, S. Schauermann,* H.-J. Freund _____ **9289 – 9293**

Influence of Carbon Deposition on the Hydrogen Distribution in Pd Nanoparticles and Their Reactivity in Olefin Hydrogenation



Asymmetric Catalysis

T. Seiser, N. Cramer* _____ **9294 – 9297**

Enantioselective C–C Bond Activation of Allenyl Cyclobutanes: Access to Cyclohexenones with Quaternary Stereogenic Centers

Chiral rhodium(I) complexes activate allenyl *tert*-cyclobutanols efficiently through enantioselective insertion into a C–C σ bond of the cyclobutane (see scheme; cod = 1,5-cyclooctadiene, DTBM = 3,5-di-*tert*-butyl-4-methoxyphenyl). Ring expansion by this method produced cyclohexenones with quaternary stereogenic centers with excellent enantioselectivity. The catalyst loading can be decreased to just 0.1 mol% in rhodium.

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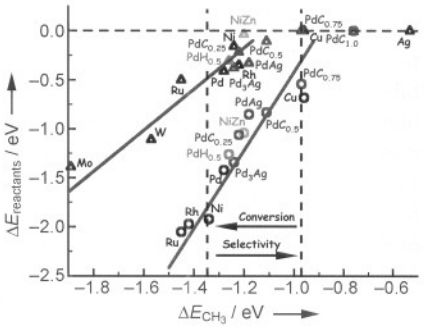
Contents

Surface Chemistry

F. Studt, F. Abild-Pedersen, T. Bligaard, R. Z. Sørensen, C. H. Christensen, J. K. Nørskov* ——— **9299 – 9302**

On the Role of Surface Modifications of Palladium Catalysts in the Selective Hydrogenation of Acetylene

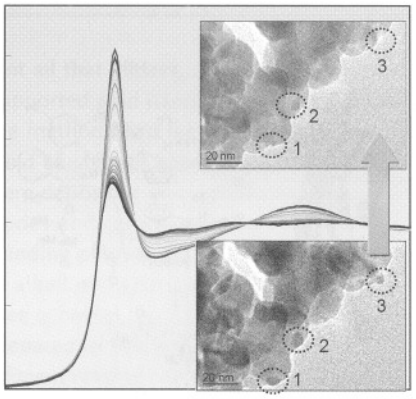


Summing Me up: DFT calculations have shown that alloying, subsurface carbon, and hydride formation, all increase the selectivity of Pd catalysts for acetylene hydrogenation by weakening the surface–adsorbate bond. A simple descriptor—the adsorption energy of a methyl group—has been used to quantify and compare the different effects in the adsorption of acetylene and ethylene on various transition-metal surfaces (see picture).

Heterogeneous Catalysis

Y. Nagai,* K. Dohmae, Y. Ikeda, N. Takagi, T. Tanabe, N. Hara, G. Guilera, S. Pascarelli, M. A. Newton, O. Kuno, H. Jiang, H. Shinjoh, S. Matsumoto ——— **9303 – 9306**

In Situ Redispersion of Platinum Autoexhaust Catalysts: An On-Line Approach to Increasing Catalyst Lifetimes?

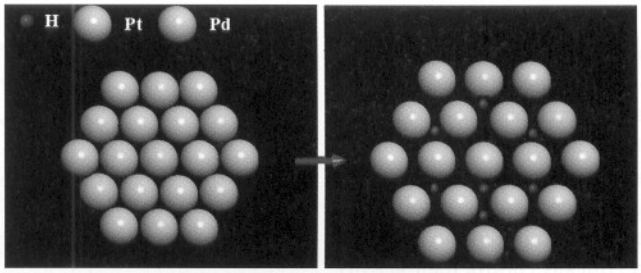


Dynamic observation: The rapid oxidative redispersion of large Pt nanoparticles supported on ceria-based oxide in auto-exhaust catalysts is demonstrated in the absence of Cl by in situ XANES analysis. An atomic migration model accounts for the observed redispersion through the trapping of Pt species at sites on the Ce support that exhibit strong interactions between the Pt oxide and the support.

Electrochemistry

S. J. Yoo, H.-Y. Park, T.-Y. Jeon, I.-S. Park, Y.-H. Cho, Y.-E. Sung* ——— **9307 – 9310**

Promotional Effect of Palladium on the Hydrogen Oxidation Reaction at a PtPd Alloy Electrode

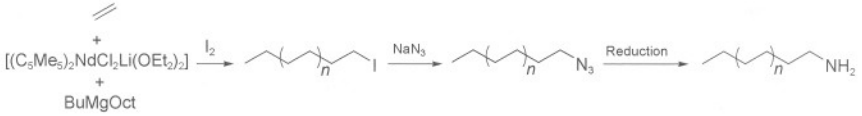


A volcano curve is observed for the hydrogen oxidation reaction (HOR) as a function of the Pd content of alloyed PtPd electrodes. The maximum exchange current density was obtained for $Pt_{72}Pd_{28}$, and the results indicate that PdH_x species (hydrogen gas spontaneously adsorbed to Pd; see picture) causes the electronic structure of Pt to be favorable for the HOR.

Reactive Polyolefins

R. Briquel, J. Mazzolini, T. Le Bris, O. Boyron, F. Boisson, F. Delolme, F. D'Agosto,* C. Boisson, R. Spitz ——— **9311 – 9313**

Polyethylene Building Blocks by Catalyzed Chain Growth and Efficient End Functionalization Strategies, Including Click Chemistry



A means to an end: Polyethylene chains obtained by catalyzed chain growth on magnesium and exhibiting molar masses up to 5000 g mol^{-1} have been end-functionalized in high yield with iodide, azide, and amine reactive end groups (see scheme). The functionalized polyethylenes can be used to generate a range of reactive polyolefins; for example, the azide-functionalized chain can undergo "click" reactions to afford macromonomers.

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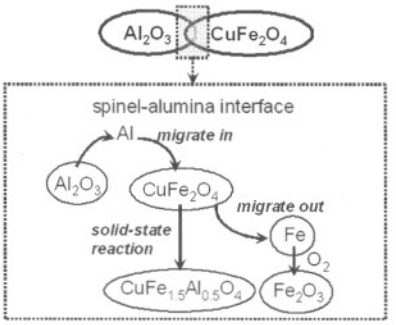
A simple thermal treatment remarkably enhances the activity and durability of $CuFe_2O_4$–Al_2O_3 composite catalysts in reforming dimethyl ether for hydrogen production. The most effective treatment temperature range is 700 to 800 °C. The active phase, $CuFe_{1.5}Al_{0.5}O_4$ formed through a solid-state reaction between $CuFe_2O_4$ and Al_2O_3, and the original phase, $CuFe_2O_4$, contribute synergistically to the enhancement.



Reforming Catalysts

K. Faungnawakij, R. Kikuchi, N. Shimoda, T. Fukunaga, K. Eguchi* ____ **9314 – 9317**

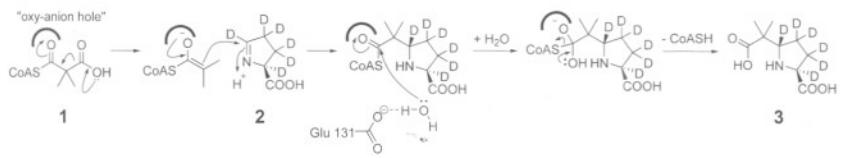
Effect of Thermal Treatment on Activity and Durability of $CuFe_2O_4$–Al_2O_3 Composite Catalysts for Steam Reforming of Dimethyl Ether

Come on allene: Commercially available $[Re_2(CO)_{10}]$ as a catalyst provides five-membered carbocycles in moderate to excellent yields with high stereoselectivity (see scheme). The configuration at each of the three sp^3 carbon centers of the ring is defined. The reaction proceeds at the β, γ, and adjacent methylene positions of the allene; previously, similar reactions usually occurred at the α, β, and γ positions of the allene.

Cycloaddition

S. Yudha S., Y. Kuninobu,* K. Takai* _____ **9318 – 9321**

Rhenium-Catalyzed Synthesis of Stereodefined Cyclopentenes from β-Ketoesters and Aliphatic Allenes

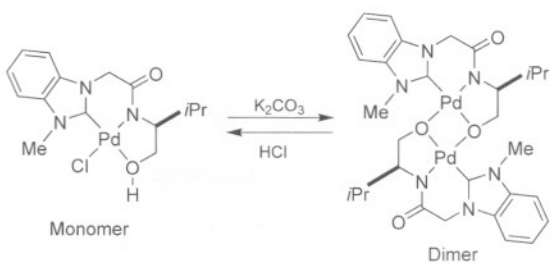


Enzyme in action: Labeling studies and the finding that carboxymethylproline synthase catalyzes production of deuterated (2*S*,5*S*)-6,6′-dimethyl-*trans*-carboxymethylproline (**3**) from dimethylmalonyl-CoA (**1**) and labeled L-pyrroline-5-carboxylate (**2**) limit possible mechanisms of C–C bond formation and thioester hydrolysis. A key feature in the catalysis is that intermediates are stabilized by hydrogen bonds in the "oxy-anion hole" of the enzyme (dark curve in scheme).

Enzyme Mechanisms

E. T. Batchelar, R. B. Hamed, C. Ducho, T. D. W. Claridge, M. J. Edelmann, B. Kessler, C. J. Schofield* _ **9322 – 9325**

Thioester Hydrolysis and C–C Bond Formation by Carboxymethylproline Synthase from the Crotonase Superfamily



Catalysts with a bite: Chiral Pd^{II} complexes were prepared with tridentate N-heterocyclic carbene amidate alkoxide ligands. Dimeric and monomeric forms were mutually convertible by acid or base treatment (see scheme). The catalysts promote asymmetric Heck reactions efficiently, offering high enantioselectivities far superior to those of existing methods.

N-Heterocyclic Carbenes

S. Sakaguchi, K. S. Yoo, J. O'Neill, J. H. Lee, T. Stewart, K. W. Jung* _____ **9326 – 9329**

Chiral Palladium(II) Complexes Possessing a Tridentate N-Heterocyclic Carbene Amidate Alkoxide Ligand: Access to Oxygen-Bridging Dimer Structures

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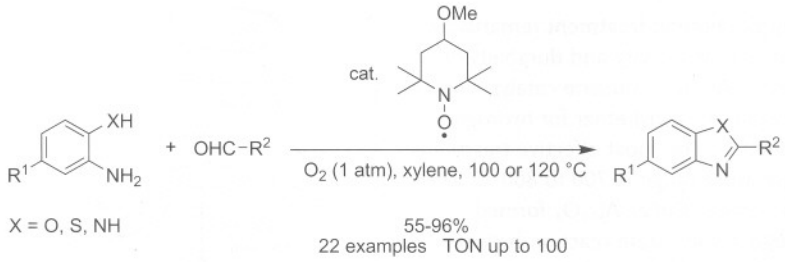
Contents

Radical Reactions

Y.-X. Chen, L.-F. Qian, W. Zhang, B. Han* ——— **9330 – 9333**

Efficient Aerobic Oxidative Synthesis of 2-Substituted Benzoxazoles, Benzothiazoles, and Benzimidazoles Catalyzed by 4-Methoxy-TEMPO

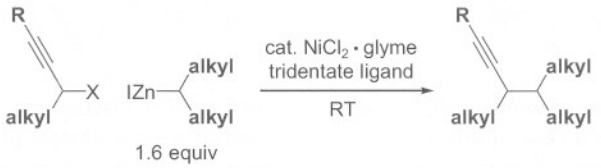


Setting the TEMPO: The scheme shows the efficient aerobic synthesis of 2-substituted benzoxazoles, benzothiazoles, and benzimidazoles where 4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy free radical (4-Methoxy-TEMPO) is used as the catalyst.

Homogeneous Catalysis

S. W. Smith, G. C. Fu* ——— **9334 – 9336**

Nickel-Catalyzed Negishi Cross-Couplings of Secondary Nucleophiles with Secondary Propargylic Electrophiles at Room Temperature

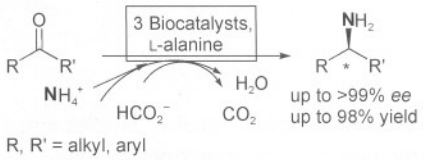


Mild thing: The first nickel-based catalysts for cross-couplings of secondary organometallic nucleophiles with secondary alkyl electrophiles have been developed. Thus, Negishi reactions proceed under mild conditions (at room temperature with no basic activators) in the presence of $NiCl_2$·glyme and a tridentate ligand (see scheme).

Chiral Amines

D. Koszelewski, I. Lavandera, D. Clay, G. M. Guebitz, D. Rozzell, W. Kroutil* ——— **9337 – 9340**

Formal Asymmetric Biocatalytic Reductive Amination

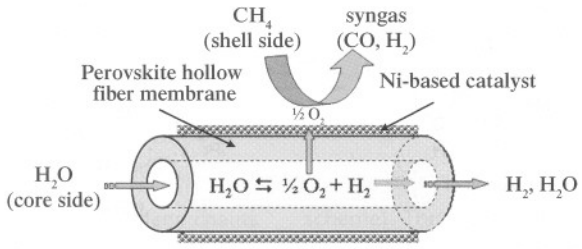


All for one: A combination of three biocatalysts (ω-transaminase, alanine dehydrogenase, and an enzyme such as formate dehydrogenase for cofactor recycling) catalyze a cascade to achieve the asymmetric transformation of a ketone into a primary α-chiral unprotected amine through a formal stereoselective reductive amination (see scheme). Only ammonia and the reducing agent (formate) are consumed during this reaction.

Hydrogen Production

H. Jiang, H. Wang,* S. Werth, T. Schiestel, J. Caro ——— **9341 – 9344**

Simultaneous Production of Hydrogen and Synthesis Gas by Combining Water Splitting with Partial Oxidation of Methane in a Hollow-Fiber Membrane Reactor



Splitting water: Oxygen-permeable perovskite hollow-fiber membranes are used to produce hydrogen and synthesis gas from water and methane (see picture). The process yields valuable compounds, and provides insight into the interplay of catalysis and separation in a membrane reactor.

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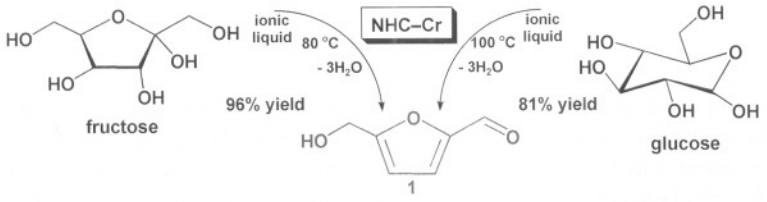
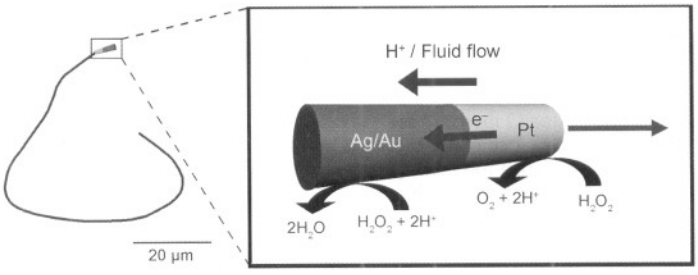


A sweet conversion! A NHC–Cr/ionic liquid system has achieved excellent efficiency and the highest 5-hydroxymethylfurfural (**1**; see scheme; NHC = N-heterocyclic carbene) yields reported thus far for both fructose and glucose feedstocks. The catalyst and ionic liquid are tolerant of high substrate loading and can be recycled after extraction of the product.

Biofuels

G. Yong, Y. Zhang,*
J. Y. Ying* ——— **9345 – 9348**

Efficient Catalytic System for the Selective Production of 5-Hydroxymethylfurfural from Glucose and Fructose



Turbo nanomotors: A dramatic increase of the speed of fuel-driven nanowire motors is obtained using an Ag/Au alloy segment. These nanomotors offer speeds as high as 150 $\mu m\,s^{-1}$ (75 body lengths per second), approaching those of the most efficient biomotors. The increase in the fuel decomposition rate associated with the electrochemical reactivity of Ag/Au alloys will enable the design of energy-efficient nanomotors.

Nanotechnology

U. K. Demirok, R. Laocharoensuk,
K. M. Manesh, J. Wang* ——— **9349 – 9351**

Ultrafast Catalytic Alloy Nanomotors

Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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