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:*

*Y. H. Kim, S. Banta**
Complete Oxidation of Methanol in an Enzymatic Biofuel Cell by a Self-Assembling Hydrogel Created from Three Modified Dehydrogenases

R. M. Culik, A. L. Serrano, M. R. Bunagan, F. Gai**
Achieving Secondary Structural Resolution in Kinetic Measurements of Protein Folding: A Case Study of the Folding Mechanism of Trp-cage

*X. Xin, M. He, W. Han, J. Jung, Z. Lin**
Low-Cost Counter Electrodes for High-Efficiency Dye-Sensitized Solar Cells

K. M. Harkness, A. Balinski, J. A. McLean, D. E. Cliffel**
Nanoscale Phase Segregation of Mixed Thiolates on Gold Nanoparticles

*S. J. Zuend, O. P. Lam, F. W. Heinemann, K. Meyer**
Insertion of Carbon Dioxide into Uranium-Activated Dicarbonyl Complexes

Y. Filinchuk, Bo Richter, T. R. Jensen,* V. Dmitriev, D. Chernyshov, H. Hagemann*
Porous and Dense $Mg(BH_4)_2$ Frameworks: Synthesis, Stability, and Reversible Absorption of Guest Species

*C. Zhang, Z. Xu, L. Zhang, N. Jiao**
Copper-Catalyzed Aerobic Oxidative Coupling of Aryl Acetaldehydes with Anilines Leading to α-Ketoamides

*A. Ardèvol, C. Rovira**
The Molecular Mechanism of Enzymatic Glycosyl Transfer with Retention of Configuration: Evidence for a Short-Lived Oxocarbenium Ion Like Species

*M. E. Weiss, E. M. Carreira**
Total Synthesis of (+)-Daphmanidin E

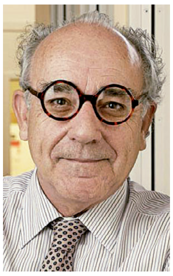
*J. Bacsa, F. Hanke, S. Hindley, R. Odrea, G. R. Darling, A. C. Jones, A. Steiner**
The Solid-State Structures of Dimethylzinc and Diethylzinc

Author Profile

"When I was eighteen I wanted to be either a physicist or a chemist.
I am waiting for the day when someone will discover a cure for Alzheimer's disease …"
This and more about Hans-Joachim (Hajo) Freund can be found on page 10016.

News

J. F. Hartwig



J. Rebek, Jr.

M. T. Reetz

Books

Contents

Fritz-Haber-Institute

History of Chemistry

B. Friedrich,* D. Hoffmann,
J. James ________ 10022 – 10049

One Hundred Years of the Fritz Haber Institute

A retrospect: The institute that was later renamed the Fritz Haber Institute began as a much-awaited remedy for the feared waning of Germany's scientific and technological superiority. The history of the Institute—from its "golden era" in the 1920s and early 1930s, through war-related research during both World Wars, crippling losses following World War II, and impressive growth since the 1950s—has largely paralleled that of 20th century Germany.

Essays

History of Chemistry

M. Dunikowska,*
L. Turko* ________ 10050 – 10062

Fritz Haber: The Damned Scientist

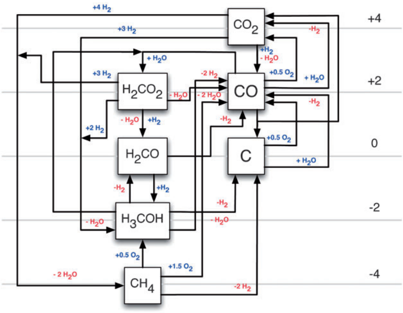
In the gallery of famous people tracing their origins to Wrocław, few are as controversial, as complex, or as tragic as Fritz Haber, ever more distant in the flux of time, yet still stirring emotions. He developed a method for the direct synthesis of ammonia from its elements and later pioneered chemical warfare on the battlefields of the First World War.

Reviews

Heterogeneous Catalysis

H.-J. Freund,* G. Meijer,* M. Scheffler,*
R. Schlögl,* M. Wolf* ____ 10064 – 10094

CO Oxidation as a Prototypical Reaction for Heterogeneous Processes



The best reference: The enormous progress in the elementary understanding of heterogeneous catalysis is based to a large degree on the study of CO oxidation as a probe reaction of heterogeneous processes. Experimental and theoretical results from this seemingly simple reaction are presented and it will be shown how these can be used to draw general conclusions about heterogeneous reactions

For the USA and Canada:
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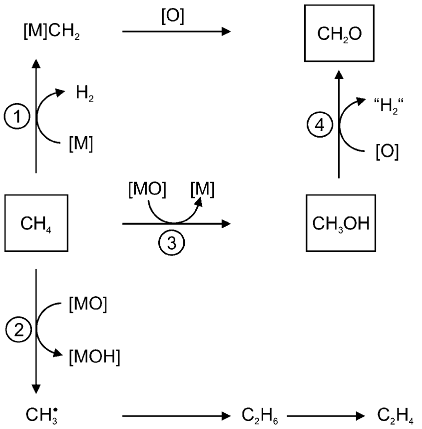
Gas-Phase Chemistry

H. Schwarz* ______ **10096 – 10115**

Chemistry with Methane: Concepts Rather than Recipes



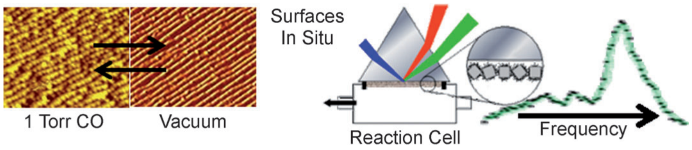
Elementary steps associated with the activation of methane are addressed from experimental and computational viewpoints; what matters most are relativistic effects, two-state reactivity scenarios, and cluster-size and ligand effects, which all play a role in the organometallic chemistry of methane at ambient conditions.

Minireviews

In Situ Analysis

G. A. Somorjai,* S. K. Beaumont, S. Alayoglu ______ **10116 – 10129**

Determination of Molecular Surface Structure, Composition, and Dynamics under Reaction Conditions at High Pressures and at the Solid–Liquid Interface



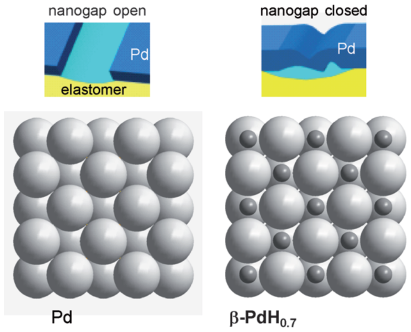
Seeing is believing: Changes in adsorbate and surface structure, composition, and dynamics are observed when such systems are studied under typical reaction conditions (see picture), either at high pressures or in the presence of liquids. Using instruments specifically designed to meet this challenge allows the exploration of interfacial phenomena under realistic conditions at the molecular level.

Highlights

Chemical Sensors

A. Gurlo,* D. R. Clarke ______ **10130 – 10132**

High-Sensitivity Hydrogen Detection: Hydrogen-Induced Swelling of Multiple Cracked Palladium Films on Compliant Substrates

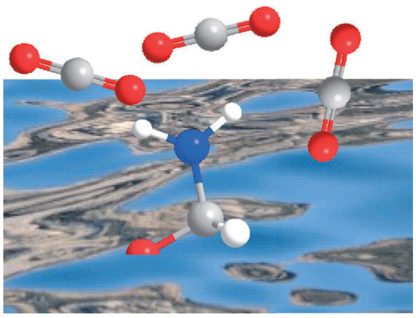


Hydrogen sponge: The reversible swelling of palladium–nickel alloys upon hydrogen absorption mechanically closes nanogaps in multiple cracked Pd–Ni films on elastomeric substrate allowing for the electric current to flow across (see picture). When the hydrogen is removed the elastomer elastically returns to its original state reopening numerous potential break junctions along each crack.

CO_2 Capture

F. Maier* ______ **10133 – 10134**

Capture of Carbon Dioxide at the Gas–Liquid Interface Elucidated by Surface Science Approaches



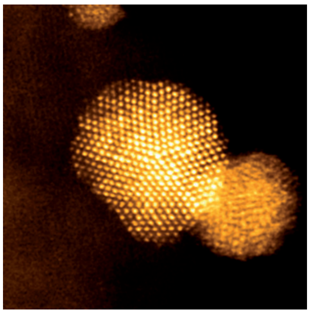
Just below the surface: New methods of photoelectron spectroscopy and the application of ionic liquids offer insight into fundamental processes in CO_2–liquid systems for carbon dioxide capture and storage, for example, the selective absorption of CO_2 in aqueous monoethanolamine (see picture; gray C, white H, blue N, red O).

Communications

Selective Oxidation

G. L. Brett, Q. He, C. Hammond,
P. J. Miedziak, N. Dimitratos, M. Sankar,
A. A. Herzing, M. Conte,
J. A. Lopez-Sanchez, C. J. Kiely,
D. W. Knight, S. H. Taylor,
G. J. Hutchings* ________ **10136–10139**

Selective Oxidation of Glycerol by Highly Active Bimetallic Catalysts at Ambient Temperature under Base-Free Conditions



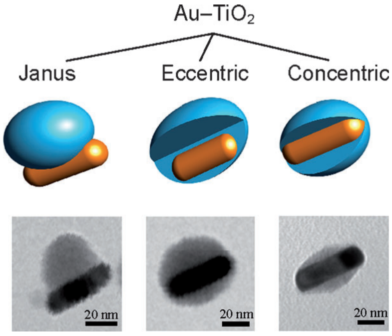
Au–Pt alloy nanoparticles deposited on $Mg(OH)_2$ (see STEM-HAADF image) show high activity in the selective oxidation of polyols using molecular oxygen as oxidant at mild and base-free conditions.

Nanostructures

Z. W. Seh, S. H. Liu, S. Y. Zhang,
M. S. Bharathi, H. Ramanarayan, M. Low,
K. W. Shah, Y. W. Zhang,*
M. Y. Han* ____________ **10140–10143**

Anisotropic Growth of Titania onto Various Gold Nanostructures: Synthesis, Theoretical Understanding, and Optimization for Catalysis

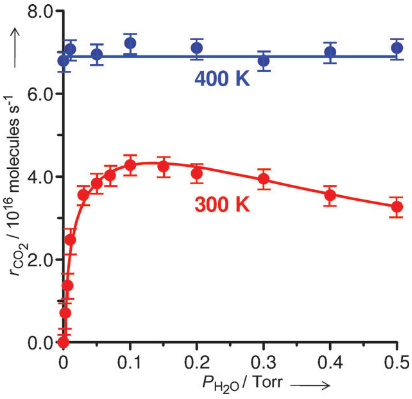
How does your garden grow? A facile method can tune the anisotropic growth of TiO_2 onto differently shaped gold nanoparticles to form Janus, eccentric, and concentric geometries (see picture). The Janus Au-TiO_2 nanostructures were found to be energetically stable using calculations, and they possess the highest catalytic activity out of all three geometries due to the highly accessible, exposed gold core on one side.



Gold Catalysis

T. Fujitani,* I. Nakamura **10144–10147**

Mechanism and Active Sites of the Oxidation of CO over Au/TiO_2



At low reaction temperatures (< 320 K), moisture plays an essential role in promoting the oxidation of CO over Au/TiO_2(110) surfaces, whereas at high temperatures (> 320 K), such promotional effect is not observed, suggesting that the mechanism and active sites of the reaction change with the reaction temperature (see picture; r_{CO_2} = rate of CO_2 formation and p_{H_2O} = pressure of H_2O).

Heterogeneous Catalysis

S. D. M. Jacques,* M. Di Michiel,
A. M. Beale,* T. Sochi, M. G. O'Brien,
L. Espinosa-Alonso, B. M. Weckhuysen,
P. Barnes ____________ **10148–10152**

Dynamic X-Ray Diffraction Computed Tomography Reveals Real-Time Insight into Catalyst Active Phase Evolution

Chemistry by color: The first dynamic study using X-ray diffraction computed tomography investigates the evolving chemistry and structural changes during the preparation of a millimeter-sized industrial hydrogenation catalyst body (see picture; time evolves from left to right, and different colors represent different phases). The method has potential for chemical imaging of materials within bulk objects undergoing physicochemical changes.

The Cluster of Excellence “Unifying Concepts in Catalysis”

offers in open competition the

Clara Immerwahr Award

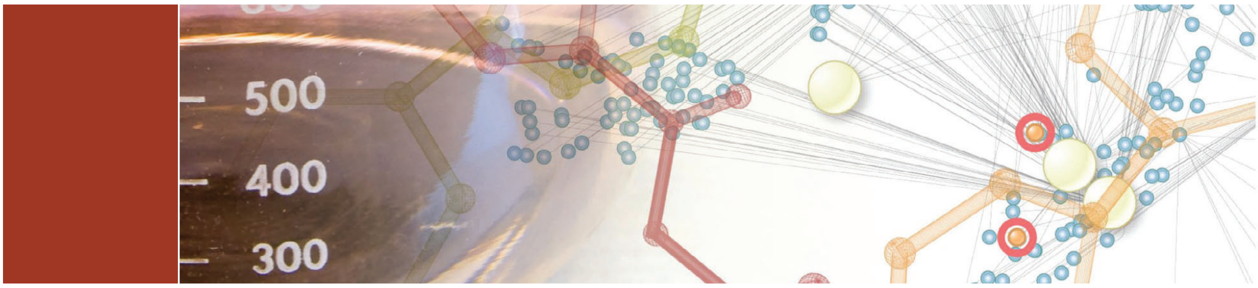
The Clara Immerwahr Award will be conferred annually to a young female scientist at an early stage of her career (postdoctoral fellow, junior researcher) for outstanding results in Catalysis Research. It is associated with a financial support of 15.000 Euro for a research stay at UniCat and thought to pave the way for setting up an independent research group in the consortium or for establishing close collaborative links with UniCat. The award is sponsored by the TU Berlin and BASF SE.

The Clara Immerwahr Award winner 2012 will be announced in December 2011 and will be honored during a public ceremony involving a guest lecture held by an internationally renowned female scientist in February 2012 at TU Berlin.

Application Documents
We expect applications of postgraduate female researchers with no restrictions to nationality or home institution who are not older than 35 years. The application must include: An application letter, a curriculum vitae, a letter containing a one page summary of the candidate‘s achievements, a project description (2 pages), a publication list, PDF files of 3 of the published papers and two letters of recommendation. The application and all submitted documents must be in English.

Application deadline: November 15, 2011

more details: www.unicat.tu-berlin.de/clara-immerwahr-award



Novartis Chemistry Lectureship

Novartis is pleased to announce the following Novartis Chemistry Lecturers for 2011 – 2012.

Yujiro Hayashi
Tokyo University of Science
Tokyo, Japan

Holger Gohlke
Heinrich-Heine-University
Düsseldorf, Germany

Ernest Giralt
IRB Barcelona and
University of Barcelona
Barcelona, Spain

Daniel Kahne
Harvard University
Cambridge, MA, USA

Melanie S. Sanford
University of Michigan
Ann Arbor, MI, USA

Tomislav Rovis
Colorado State University
Fort Collins, CO, USA

The Novartis Chemistry Lectureship is awarded to scientists in recognition of outstanding contributions to organic and computational chemistry, including applications to biology.

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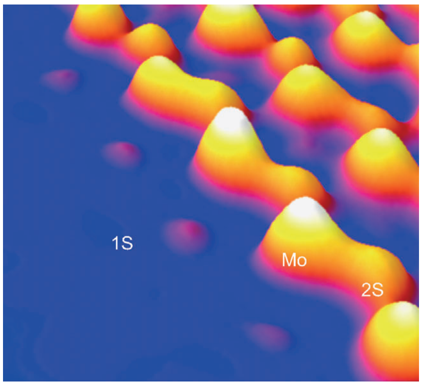
High-Resolution Microscopy

L. P. Hansen, Q. M. Ramasse,
C. Kisielowski, M. Brorson, E. Johnson,
H. Topsøe, S. Helveg* ___ **10153 – 10156**

Atomic-Scale Edge Structures on Industrial-Style MoS_2 Nanocatalysts

Atoms on the edge: The atomic edge structure of industrial-style MoS_2 nanocatalysts was imaged using single-atom sensitive electron microscopy (see picture). The observed industrial-style edge terminations match predictions of model catalyst studies and thus address the so-called "materials gap" in catalysis.

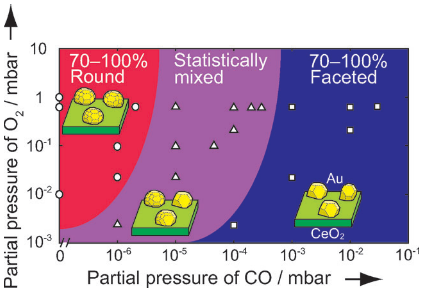


Gold Catalysis

T. Uchiyama, H. Yoshida, Y. Kuwauchi,
S. Ichikawa, S. Shimada, M. Haruta,
S. Takeda* ___ **10157 – 10160**

Systematic Morphology Changes of Gold Nanoparticles Supported on CeO_2 during CO Oxidation

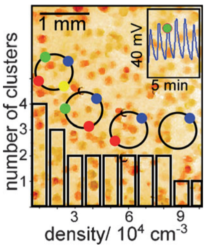
The morphology of gold nanoparticles (GNPs) supported on CeO_2 in various partial pressures of CO and O_2 is presented; their morphology correlates well with their catalytic activity. Adsorbed CO molecules stabilize the major {111} and {100} facets of GNP polyhedra and dissociation of O_2 molecules may occur at the perimeter interface of GNPs and CeO_2 supports with the aid of electron irradiation, thus causing rounded morphology of the GNPs (see diagram).



Phase Clusters

A. F. Taylor, M. R. Tinsley, F. Wang,
K. Showalter* ___ **10161 – 10164**

Phase Clusters in Large Populations of Chemical Oscillators



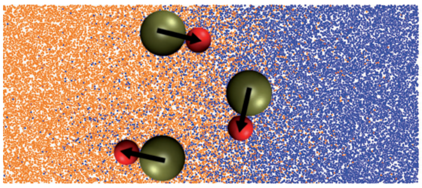
Complex synchronization: Chemical oscillators communicating by exchange of intermediate species through the surrounding solution form clusters of individuals with synchronized oscillations that are out of phase with other clusters. The system evolves from unsynchronized oscillations at low number density n to four, three, two, and finally one cluster with increasing n (see picture).

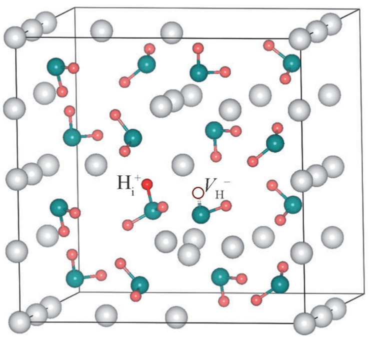
Nanomotors

S. Thakur, J.-X. Chen,
R. Kapral* ___ **10165 – 10169**

Interaction of a Chemically Propelled Nanomotor with a Chemical Wave

A chemically powered nanodimer motor interacting with a chemical wave results in the deflection of the nanomotor (see picture). Such an effect provides a possible mechanism for the control of nanomotor motion.



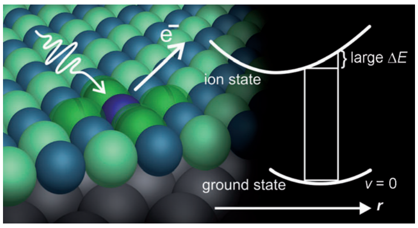


A question of size: $LiNH_2$ decomposes into Li_2NH and NH_3 through two competing mechanisms, one that involves the formation of native defects in the interior of the material (by a Frenkel pair mechanism) and the other at the surface (see picture; H red, Li gray, N blue). The prevailing mechanism and hence the activation energy thus depend on the surface-to-volume ratio, or the specific surface area, which changes with the particle size.

Hydrogen Storage

K. Hoang, A. Janotti,
C. G. Van de Walle* ______ **10170–10173**

The Particle-Size Dependence of the Activation Energy for Decomposition of Lithium Amide

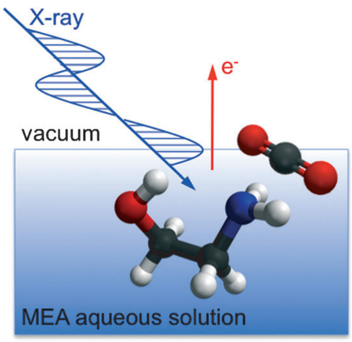


Breathing: A simple and intuitive approach relates changes in bond lengths of core-hole ionized states to the extent of vibrational fine structure, or Franck–Condon broadening (ΔE), in X-ray photoelectron spectra of ionic compounds. For the extreme case of a monolayer of MgO on Ag(100), the difference in Franck–Condon broadening compared to bulk MgO reflects the different binding situation in the supported oxide (see picture, r = Mg–O distance).

Photoelectron Spectroscopy

C. J. Nelin, P. S. Bagus,* M. A. Brown,
M. Sterrer, H.-J. Freund __ **10174–10177**

Analysis of the Broadening of X-ray Photoelectron Spectroscopy Peaks for Ionic Crystals



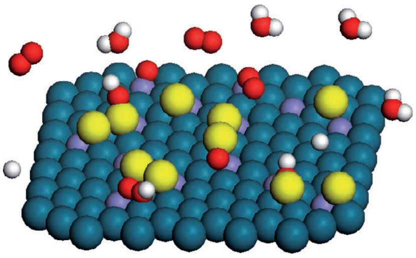
Interface matters! Photoelectron spectra of aqueous solutions of monoethanolamine (MEA) that had been treated with CO_2 were used to determine the spatial distribution of MEA and the reaction products with respect to the solution interface (see picture). Neutral MEA shows a propensity for the solution surface, whereas protonated MEA and the reaction products prefer bulk solvation.

CO_2 Capture

T. Lewis, M. Faubel, B. Winter,
J. C. Hemminger* ______ **10178–10181**

CO_2 Capture in Amine-Based Aqueous Solution: Role of the Gas–Solution Interface

Working together: $Pd_{0.9}Fe_{0.1}$–$Pd_3Fe(111)$ (see picture, Pd adatoms yellow, Fe purple, Pd blue-green, O red, H white) displays enhanced performance for the oxygen reduction reaction with five to eight times higher activity than Pd(111). The high catalytic activity may originate from a cooperative effect of a segregated Pd layer with its large tendency to remove surface O species by protonation and active Fe with its ability to dissociate O_2.



Electrocatalysis

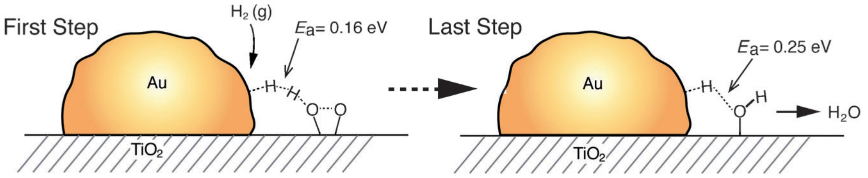
X. Yang, J. Hu, J. Fu, R. Wu,
B. E. Koel* ____________ **10182–10185**

Role of Surface Iron in Enhanced Activity for the Oxygen Reduction Reaction on a $Pd_3Fe(111)$ Single-Crystal Alloy

Gold Catalysis

I. X. Green, W. Tang, M. Neurock,
J. T. Yates, Jr.* ________ **10186 – 10189**

Low-Temperature Catalytic H_2 Oxidation over Au Nanoparticle/TiO_2 Dual Perimeter Sites

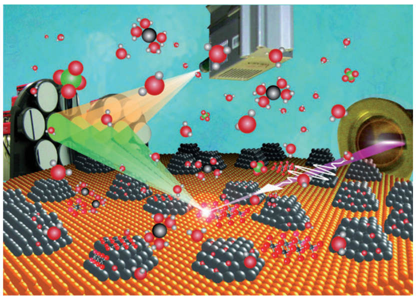


The catalytic reaction of H_2+O_2 over a Au/TiO_2 catalyst was studied by transmission IR spectroscopy and DFT calculations. A reaction path of O_2-assisted H_2 dissociation at the Au/TiO_2 dual perimeter site was found to proceed through a Ti–OOH intermediate (see scheme). The calculated barrier range (0.13–0.25 eV) for the sequence of low-energy steps agree with the experimental E_a of 0.22 eV.

Fuel Cell Catalysis

D. Friebel,* D. J. Miller, D. Nordlund,
H. Ogasawara,
A. Nilsson* ________ **10190 – 10192**

Degradation of Bimetallic Model Electrocatalysts: An In Situ X-Ray Absorption Spectroscopy Study

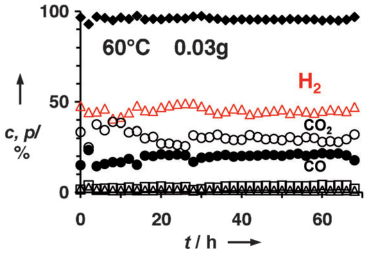


Gold support destabilizes platinum: Driven by the low surface energy of Au, a Pt fuel cell catalyst is removed from the surface of the Au support. Depending on the electrochemical potential, this removal can occur through Pt dissolution either into the Au substrate or into the electrolyte (see picture). In situ HERFD XAS measurements indicate formation of PtO_2 by a dissolution–precipitation mechanism.

Heterogeneous Catalysis

C. Pirez, M. Capron, H. Jobic,
F. Dumeignil,
L. Jalowiecki-Duhamel* __ **10193 – 10197**

Highly Efficient and Stable $CeNiH_ZO_Y$ Nano-Oxyhydride Catalyst for H_2 Production from Ethanol at Room Temperature

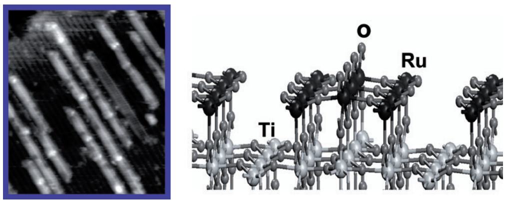


The $CeNiH_ZO_Y$ oxyhydride compound is an exceptional catalyst that totally converts ethanol at 60 °C and produces H_2 in the presence of water and oxygen. The H_2 fraction of the gas-phase products is about 50 % (see picture; *c*: conversion, *p*: production). The oxyhydride compound is formed by in-situ activation of $CeNiO_Y$ with H_2 at 250 °C. The presence of hydride species in the catalyst is evidenced by inelastic neutron scattering.

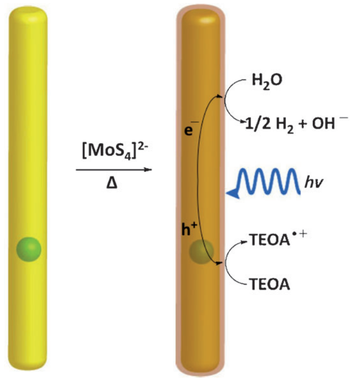
Heterogeneous Catalysis

F. Yang, S. Kundu, A. B. Vidal, J. Graciani,
P. J. Ramírez, S. D. Senanayake,
D. Stacchiola, J. Evans, P. Liu, J. F. Sanz,
J. A. Rodriguez* ________ **10198 – 10202**

Determining the Behavior of RuO_x Nanoparticles in Mixed-Metal Oxides: Structural and Catalytic Properties of RuO_2/TiO_2(110) Surfaces



Hot off the wire: Scanning tunneling microscopy, X-ray photoelectron spectroscopy, and density functional calculations were used to study the interaction of RuO_2 nanostructures with TiO_2(110). Ruthenium oxide forms unique Ru_3O_6 wire-like structures on TiO_2 that can be easily reduced and re-oxidized at temperatures in the range of 400–600 K, and it has a very high catalytic activity for the low-temperature oxidation of CO.

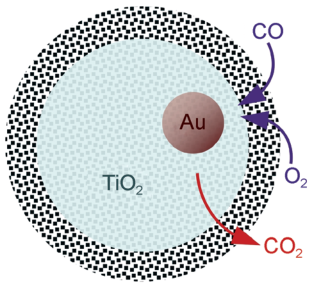


Light–water reactor: An amorphous molybdenum sulfide species structurally similar to reduced MoS_3 is shown to be photocatalytically active for hydrogen generation from H_2O with visible light (see picture; TEOA = triethanolamine). Thermally deposited in one step, MoS_3 is photosensitized by quantum-controlled semiconductor nanocrystals that serve as model systems for the photophysics of solar fuel generation.

Nanoparticle Photocatalysis

M. L. Tang, D. C. Grauer,
B. Lassalle-Kaiser, V. K. Yachandra,
L. Amirav, J. R. Long, J. Yano,
A. P. Alivisatos* ———— **10203 – 10207**

Structural and Electronic Study of an Amorphous MoS_3 Hydrogen-Generation Catalyst on a Quantum-Controlled Photosensitizer

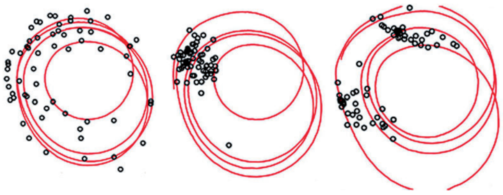


Trapped inside: A new catalyst was developed where gold nanoparticles are encased inside hollow titania nanospheres (see picture). The new nanoarchitecture prevents the nanoparticles from sintering and losing their activity while still providing the reactants free access to the metal surface. The result is a catalyst capable of promoting the oxidation of CO at room temperature while surviving calcination at temperatures above 775 K.

Gold Nanoparticles

I. Lee, J. B. Joo, Y. Yin,
F. Zaera* ———— **10208 – 10211**

A Yolk@Shell Nanoarchitecture for Au/TiO_2 Catalysts

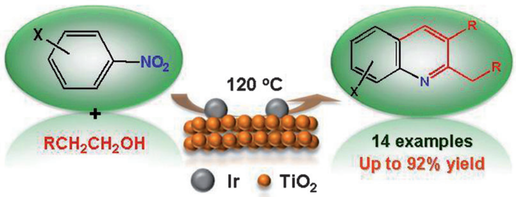


Dialing up complex dynamic structures: A population of 64 chaotic chemical oscillators (phase–space snapshots, left) in a nickel electrodissolution is steered with mild global feedback to one (middle) and two (right) clustered states.

Complex Dynamic Structures

C. G. Rusin, I. Tokuda, I. Z. Kiss,
J. L. Hudson* ———— **10212 – 10215**

Engineering of Synchronization and Clustering of a Population of Chaotic Chemical Oscillators



A versatile heterogeneous catalyst consisting of sub-nanosized iridium clusters deposited on titania (Ir/TiO_2-NCs) promotes the direct tandem synthesis of quinoline derivatives from readily available nitroarenes and aliphatic alcohols under mild and additive-free conditions (see scheme). The process tolerates the presence of various reactive functional groups and is highly selective.

Heterogeneous Catalysis

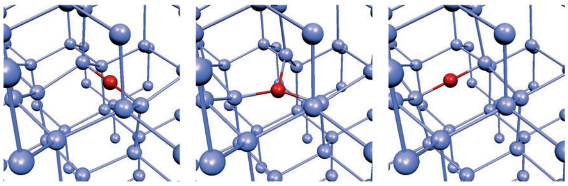
L. He, J. Q. Wang, Y. Gong, Y. M. Liu,
Y. Cao,* H. Y. He,
K. N. Fan ———— **10216 – 10220**

Titania-Supported Iridium Subnanoclusters as an Efficient Heterogeneous Catalyst for Direct Synthesis of Quinolines from Nitroarenes and Aliphatic Alcohols

Silicon Defects

S. K. Estreicher,* D. J. Backlund,
C. Carbogno, M. Scheffler **10221 – 10225**

Activation Energies for Diffusion of Defects in Silicon: The Role of the Exchange-Correlation Functional

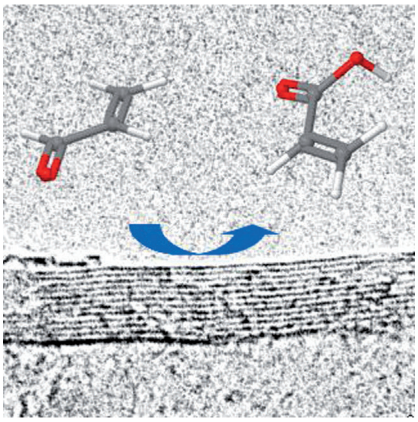


DFT calculations were used to determine the activation energies (E_a values) for the diffusion of defects such as O atoms (O_i^0 red sphere in the picture) in silicon (blue spheres). The migration paths were obtained from the nudged elastic band method. The activation energies calculated with four exchange-correlation functionals (E_{xc}) were compared to experimental data. The E_a values of "atomic-like" interstitials are mostly independent of E_{xc}, but those of strongly bound impurities are sensitive to the choice of E_{xc}.

Metal-Free Catalysis

B. Frank, R. Blume, A. Rinaldi,
A. Trunschke,* R. Schlögl **10226 – 10230**

Oxygen Insertion Catalysis by sp^2 Carbon



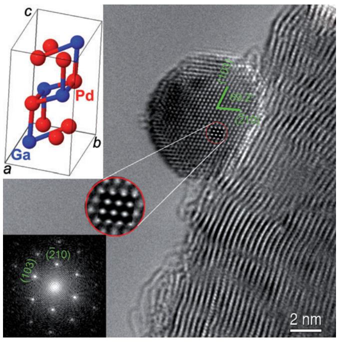
Black matter in catalysis: Graphitic carbon catalyzes the insertion of O atoms into acrolein. Such complex multistep atom rearrangements were believed to be the exclusive domain of metal (oxide) catalysis. In the C-catalyzed process, the nucleophilic O atoms terminating the graphite (0001) surface abstract the formyl H atom and the activated aldehyde is oxidized by a mobile epoxide O atom. Thus, the sp^2 carbon acts as a bifunctional catalyst.

Nanostructured Catalysts

L. Shao, W. Zhang, M. Armbrüster,
D. Teschner, F. Girgsdies, B. Zhang,
O. Timpe, M. Friedrich, R. Schlögl,
D. S. Su* ———————— **10231 – 10235**

Nanosizing Intermetallic Compounds Onto Carbon Nanotubes: Active and Selective Hydrogenation Catalysts

Nanosized, yet ordered: Active and selective Pd$_2$Ga intermetallic compounds supported on carbon nanotubes have been synthesized and applied to alkyne hydrogenation. Intermetallic compounds on the nanoscale are necessary to achieve high mass activity, whereas ordered structures within intermetallic compounds form high barriers for subsurface chemistry and prevent large active ensembles on Pd surface.

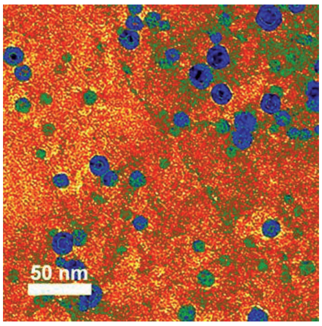


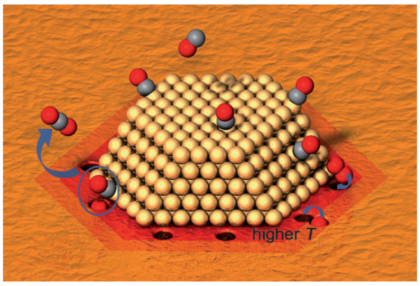
Iron Oxide Nanostructures

Y. Gao, D. Ma,* G. Hu, P. Zhai, X. Bao,
B. Zhu, B. Zhang,
D. S. Su* ———————— **10236 – 10240**

Layered-Carbon-Stabilized Iron Oxide Nanostructures as Oxidation Catalysts

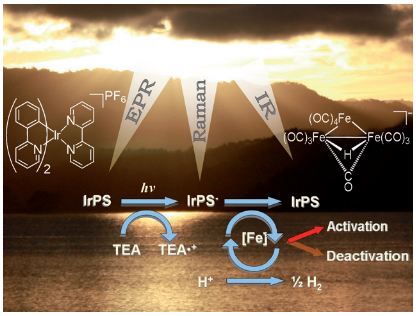
Into the layer: Layered carbon–iron oxide nano-composites catalysts are very active in catalytic oxidation reactions. The size and structure of the iron oxide nanoparticles (blue in the TEM image) embedded in the layered carbon can be controlled very simply by changing the temperature of the synthesis reaction.





Ideal location: The active oxygen for CO oxidation on Au/TiO_2 catalysts is a highly stable oxygen species, whose formation is facile and hardly activated. This species is proposed to be surface lattice oxygen at the perimeter of the Au–TiO_2 interface, activated by the presence of the Au nanoparticle. At higher temperatures, thermally activated O_{latt} migration also gives access to adjacent O_{latt} species.

Active Oxygen



Light on the water: The coupling of Raman and EPR spectroscopy was crucial in the study of the activation, operation, and deactivation steps in the light-driven splitting of water catalyzed by iridium and iron. The results may provide the foundation for improved water-reduction catalysts. IrPS = iridium photosensitizer, TEA = triethylamine.

Reaction Mechanisms

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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