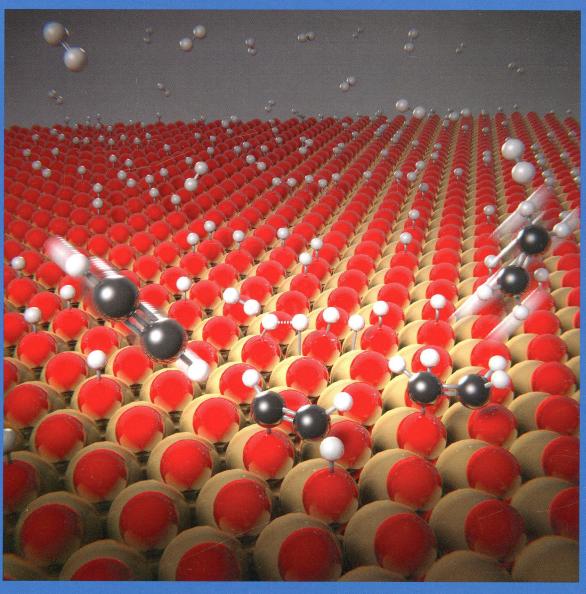


VOLUME 118 NUMBER 10

pubs.acs.org/JPCC

THE JOURNAL OF PHYSICAL CHEMISTRY C



The Hydrogenation **Playground on Ceria** (see page 5352)

ENERGY CONVERSION AND STORAGE, OPTICAL AND ELECTRONIC DEVICES, INTERFACES, NANOMATERIALS, AND HARD MATTER



THE JOURNAL OF PHYSICAL CHEMISTRY

MARCH 13, 2014 VOLUME 118 ISSUE 10

JPCCCK 118(10) 5061-5614 (2014)

ISSN 1932-7447 Registered in the U.S. Patent and Trademark Office © 2014 by the American Chemical Society

ON THE COVER: The hydrogenation playground on ceria. Ceria is a key component in many heterogeneous catalysts. In typical applications, ceria magnifies the performance of the active phase, but the stand-alone catalytic function of ceria is rare and usually related to oxidations. Interestingly, we reported an unprecedented performance of pure ceria for the partial hydrogenation of acetylene to ethylene with outstanding selectivity. Experimental evidence shows that (111) facets are especially prone to hydrogenation. We combine in-depth characterization, catalytic tests, and density-functional theory mechanistic studies to provide a molecular-level understanding of the hydrogenation of acetylene on the CeO₂(111) surface. Acetylene adsorption leads to the formation of highly reactive C₂H₂ radical species that are hydrogenated to form C₂H₃ with no barrier at large H₂/C₂H₂ ratios. The high alkene selectivity is owed to the lower activation barrier for subsequent hydrogenation, leading to gas-phase ethylene compared with that for the formation of adsorbed C2H4 radical species that would enable complete hydrogenation. Our results open exciting perspectives for investigating the ability of pure ceria as a catalyst for the selective hydrogenation of alkynes and other functional groups. Cover art was created with the help of Enrique Sahagún (www.scixel.es). See page 5352.

Articles Energy Conversion and Storage; Energy and Charge Transport 5061 dx.doi.org/10.1021/jp4098638 Structure and Dynamics of an Electrolyte Confined in Charged Nanopores Pierre-Andre Cazade, Remco Hartkamp, and Benoit Coasne* 5073 dx.doi.org/10.1021/jp409962x Ab Initio Calculation of Proton Transport in DvPO. Isaac M. Markus, Nicole Adelstein, Mark Asta,* and Lutgard C. De Jonghe 5081 dx.doi.org/10.1021/jp410262t Palladium Clusters Anchored on Graphene Vacancies and Their Effect on the Reversible Adsorption of Hydrogen María J. López,* Iván Cabria, and Julio A. Alonso 5091 dx.doi.org/10.1021/jp410550v Vacuum Topotactic Conversion Route to Mesoporous Orthorhombic MoO₃ Nanowire Bundles with Enhanced **Electrochemical Performance** Zhengqiu Yuan, Lulu Si, Denghu Wei, Lei Hu, Yongchun Zhu,* Xiaona Li, and Yitai Qian*

dx.doi.org/10.1021/jp410676b

5102 Carbon Support Effects on the Hydrogen Storage Properties of LiBH₄ Nanoparticles: A First-Principles Study Ebrahim Hazrati,* Geert Brocks, and Gilles A. de Wijs*



Polyamorphism and Pressure-Induced Metallization at the Rigidity Percolation Threshold in Densified GeSe. Glass Bora Kalkan,* Ranga P. Dias, Choong-Shik Yoo, Simon M. Clark, and Sabyasachi Sen

5122

dx.doi.org/10.1021/jp410999b

Theory of Anomalous Dynamics of Electric Double Layer at Heterogeneous and Rough Electrodes Maibam Birla Singh and Rama Kant*

5134

dx.doi.org/10.1021/jp411076a

Correlation between Capacitance and Porosity in Microporous Carbon Monoliths

A. Garcia-Gomez, V. Barranco, G. Moreno-Fernandez, J. Ibañez, T. A. Centeno, and J. M. Rojo*

5142

dx.doi.org/10.1021/jp4110773

Quantum-Dot-Sensitized Solar Cells with Water-Soluble and Air-Stable PbS Quantum Dots Askhat N. Jumabekov, Felix Deschler, Daniel Böhm, Laurence M. Peter, Jochen Feldmann, and Thomas Bein*

5150

dx.doi.org/10.1021/jp411377r

Time-of-Flight Current Shapes in Molecularly Doped Polymers: Effects of Sample Thickness and Irradiation Side and Carrier Generation Width

Andrey P. Tyutney, David S. Weiss,* David H. Dunlap, and Vladimir S. Saenko

5159

dx.doi.org/10.1021/jp411653s

Energy Transfer from C-Phycocyanin to Single-Walled Carbon Nanotubes

Karim El Hadi, Patricia Bertoncini,* and Olivier Chauvet

5164

Crystalline Si/Graphene Quantum Dots Heterojunction Solar Cells

dx.doi.org/10.1021/jp412591k

Peng Gao, Ke Ding, Yan Wang, Kaigun Ruan, Senlin Diao, Qing Zhang, Baoquan Sun,* and Jiansheng Jie*

5172

dx.doi.org/10.1021/jp412594b

Enhanced Electron Field Emission of One-Dimensional Highly Protruded Graphene Wrapped Carbon Nanotube Composites Pranati Nayak, P. N. Santhosh, and S. Ramaprabhu*

5180

dx.doi.org/10.1021/jp412771f

Diffusion Path and Conduction Mechanism of Protons in Hydroxyapatite Masatomo Yashima,* Naoyuki Kubo, Kazuki Omoto, Hirotaka Fujimori, Kotaro Fujii, and Kenji Ohoyama

5188

dx.doi.org/10.1021/jp4128176

A Simple Kinetic Model for Singlet Fission: A Role of Electronic and Entropic Contributions to Macroscopic Rates Anatoly B. Kolomeisky,* Xintian Feng, and Anna I. Krylov*

dx.doi.org/10.1021/jp500547i

Reduced Bimolecular Charge Recombination Loss in Thermally Annealed Bilayer Heterojunction Photovoltaic Devices with Large External Quantum Efficiency and Fill Factor Bin Yang, Yongbo Yuan, and Jinsong Huang*

5203

dx.doi.org/10.1021/jp500593d

Chloroaluminate-Doped Conducting Polymers as Positive Electrodes in Rechargeable Aluminum Batteries Nicholas S. Hudak*

5216

dx.doi.org/10.1021/jp500755t

Diffusion of Oxygen in Ceria at Elevated Temperatures and Its Application to H₂O/CO₂ Splitting Thermochemical Redox Cycles

Simon Ackermann, Jonathan R. Scheffe,* and Aldo Steinfeld

Surfaces, Interfaces, Porous Materials, and Catalysis

5226

dx.doi.org/10.1021/jp407865e

Combined Density Functional Theory and Kinetic Monte Carlo Study of Selective Oxidation of NH2 on Rutile RuO2(110) at **Ambient Pressures**

Sved Islamuddin Shah,* Samovo Hong, and Talat S. Rahman

5239 0 dx.doi.org/10.1021/ip4088964

Effective One-Step Synthesis of Silica Supported 1,3-Dibutylimidazolium Acetate for Carbon Dioxide Capture Preston M. MacQueen, Ryan A. Bach, Christopher T. P. MacLean, and Stephanie L. MacQuarrie*

5243

dx.doi.org/10.1021/ip409447u

Insight into the Effect of Promoter Mn on Ethanol Formation from Syngas on a Mn-Promoted MnCu(211) Surface: A Comparison with a Cu(211) Surface

Riguang Zhang, Guiru Wang, Baojun Wang,* and Lixia Ling

5255

dx.doi.org/10.1021/jp409847v

Supramolecular and Chiral Effects at the Titanyl Phthalocyanine/Ag(100) Hybrid Interface

Stefano Colonna,* Giuseppe Mattioli,* Paola Alippi, Aldo Amore Bonapasta, Antonio Cricenti, Francesco Filippone, Paola Gori, Anna Maria Paoletti, Giovanna Pennesi, Fabio Ronci, and Gloria Zanotti

5268

dx.doi.org/10.1021/jp410003e

Crucial Role of Surfactants in Bubble-Propelled Microengines Hong Wang, Guanjia Zhao, and Martin Pumera*

5275

dx.doi.org/10.1021/jp4100262

Additive Electron Pathway and Nonadditive Molecular Conductance by Using a Multipodal Bridging Compound Manabu Kiguchi,* Yuuta Takahashi, Shintaro Fujii, Masayoshi Takase, Tomoyuki Narita, Masahiko Iyoda,* Masayo Horikawa, Yasuhisa Naitoh, and Hisao Nakamura*

5284

dx.doi.org/10.1021/jp4107469

Systematic Control of Hole-Injection Barrier Height with Electron Acceptors in [7] phenacene Single-Crystal Field-Effect

Xuexia He, Shino Hamao, Ritsuko Eguchi, Hidenori Goto, Yukihiro Yoshida, Gunzi Saito, and Yoshihiro Kubozono*

5794

dx.doi.org/10.1021/jp410780n

Mechanism of Low Schottky Barrier Formation for Chromium/CdZnTe Contact

Shouzhi Xi, Wangi Jie, * Ganggiang Zha, * Wenhua Zhang, Junfa Zhu, Xuxu Bai, Tao Feng, Ning Wang, Fan Yang, and Rui Yang

5299

dx.doi.org/10.1021/ip410911i

Graphene Oxide as a Surfactant and Support for In-Situ Synthesis of Au-Pd Nanoallovs with Improved Visible Light Photocatalytic Activity

Yanhui Zhang, Nan Zhang, Zi-Rong Tang, and Yi-Jun Xu*

5309 6

dx.doi.org/10.1021/ip410947d

Mechanistic Investigation of the Catalytic Decomposition of Ammonia (NH₂) on an Fe(100) Surface: A DFT Study Sang Chul Yeo, Sang Soo Han, and Hvuck Mo Lee*

5317

dx.doi.org/10.1021/jp4109706

Reactivity of CO on Carbon-Covered Cobalt Surfaces in Fischer-Tropsch Synthesis

Lennart Joos, Ivo A. W. Filot, Stefaan Cottenier, Emiel J. M. Hensen, Michel Waroquier, Veronique Van Speybroeck, and Rutger A. van Santen*

5328

dx.doi.org/10.1021/jp411062u

Superhydrophobicity and Optical Transparency in Thin Films: Criteria for Coexistence

Chang Wang, Alex H. F. Wu, and Robert N. Lamb*

5336

dx.doi.org/10.1021/jp411219z

Local Structure of Fe Impurity Atoms in ZnO: Bulk versus Surface

J. A. McLeod, * D. W. Boukhvalov, D. A. Zatsepin, R. J. Green, B. Leedahl, L. Cui, E. Z. Kurmaev, I. S. Zhidkov, L. D. Finkelstein, N. V. Gavrilov, S. O. Cholakh, and A. Moewes

5346

dx.doi.org/10.1021/jp411256q

Single-Layer MoS₂ with Sulfur Vacancies: Structure and Catalytic Application

Duy Le, Takat B. Rawal, and Talat S. Rahman*

5352

dx.doi.org/10.1021/jp410478c

Molecular-Level Understanding of CeO₂ as a Catalyst for Partial Alkyne Hydrogenation
Javier Carrasco,* Gianvito Vilé, Delia Fernández-Torre, Rubén Pérez, Javier Pérez-Ramírez,* and M. Verónica Ganduqlia-Pirovano

5361

dx.doi.org/10.1021/jp411469u

Effects of Composition of Oligo(ethylene glycol)-Based Mixed Monolayers on Peptide Grafting and Human Immunoglobulin Detection

Nafisa Islam, Patrick V. Gurgel, Orlando J. Rojas, and Ruben G. Carbonell*

5374

dx.doi.org/10.1021/jp4118634

Importance of a Nonlocal Description of Electron–Electron Interactions in Modeling the Dissociative Adsorption of H_2 on Cu(100)

Florian Göltl, Céline Houriez, Marie Guitou, Gilberte Chambaud,* and Philippe Sautet*

5383

dx.doi.org/10.1021/jp4122326

High-Throughput Screening of Porous Crystalline Materials for Hydrogen Storage Capacity near Room Temperature Yamil J. Colón, David Fairen-Jimenez, Christopher E. Wilmer, and Randall Q. Snurr*

5390

dx.doi.org/10.1021/jp412461q

Chemical Reaction Mechanism of Polytetrafluoroethylene on Aluminum Surface under Friction Condition
Tasuku Onodera,* Kenji Kawasaki, Takayuki Nakakawaii, Yuji Higuchi, Nobuki Ozawa, Kazue Kurihara, and Momoji Kubo

5397

0

dx.doi.org/10.1021/jp412433a

Water Adsorption in Flexible Gallium-Based MIL-53 Metal—Organic Framework
François-Xavier Coudert, Aurélie U. Ortiz, Volker Haigis, David Bousquet, Alain H. Fuchs, Anthony Ballandras, Guy Weber,
Igor Bezverkhyy, Nicolas Geoffroy, Jean-Pierre Bellat, Guillaume Ortiz, Gérald Chaplais, Joël Patarin, and Anne Boutin*

5406

dx.doi.org/10.1021/jp4126073

Influence of Surface Roughening of Rutile Single-Crystalline TiO_2 on Photocatalytic Activity for Oxygen Photoevolution from Water in Acidic and Alkaline Solutions

Etsushi Tsuji, Ken-ichi Fukui, and Akihito Imanishi*

5414

dx.doi.org/10.1021/jp5002308

Calculated Stability and Structure of Nickel Ferrite Crystal Surfaces in Hydrothermal Environments Christopher J. O'Brien,* Zs. Rák, and Donald W. Brenner

5424

8

dx.doi.org/10.1021/jp500322p

Phenomenological Kinetics of the Carbonation Reaction of Lithium Hydroxide Monohydrate: Role of Surface Product Layer and Possible Existence of a Liquid Phase

Yusuke Noda and Nobuyoshi Koga*

Plasmonics, Optical Materials, and Hard Matter 5445 dx.doi.org/10.1021/ip4076383 Structure Evolutions and Metallic Transitions in In-Se- Under High Pressure Jinggeng Zhao* and Liuxiang Yang* CAED dx.doi.org/10.1021/jp411371g Stacked Gold Nanorectangles with Higher Order Plasmonic Modes and Top-Down Plasmonic Coupling Sidney T. Malak, Tobias König, Rachel Near, Zachary A. Combs, Mostafa A. El-Sayed, and Vladimir V. Tsukruk* 5463 dx.doi.org/10.1021/ip411503s Structure, Magnetism, and Valence States of Cobalt and Platinum in Quasi-One-Dimensional Oxides A-CoptOs with A = Ca. D. Mikhailova, * C. Y. Kuo, P. Reichel, A. A. Tsirlin, A. Efimenko, M. Rotter, M. Schmidt, Z. Hu, T. W. Pi, L. Y. Jang, Y. L. Soo, S. Oswald. and L. H. Tieng 5470 dx.doi.org/10.1021/jp412129m

Symmetry Lowering in Triindoles: Impact on the Electronic and Photophysical Properties Constanza Ruiz, Eva M. García-Frutos, Demetrio A. da Silva Filho, Juan T. López Navarrete,* M. Carmen Ruiz Delgado,* and Berta Gómez-Lor*

Scaling of the Surface Plasmon Resonance in Gold and Silver Dimers Probed by EELS Shima Kadkhodazadeh,* Jakob Rosenkrantz de Lasson, Marco Beleggia, Harald Kneipp, Jakob Birkedal Wagner, and Katrin Kneipp

5486 dx.doi.org/10.1021/ip500492k

Phase-Modified Up-Conversion Luminescence in Er-Doped Single-Crystal PbTiO₃ Nanofibers Siyu Gong, Zhaohui Ren,* Shan Jiang, Ming Li, Xiang Li, Xiao Wei, Gang Xu, Ge Shen, and Gaorong Han*

5494

Influence of Dielectric Anisotropy on the Absorption Properties of Localized Surface Plasmon Resonances Embedded in Si

Li-Wei Chou, Rachel D. Near, Dmitriy S. Boyuk, and Michael A. Filler*

Identifying Trapped Electronic Holes at the Aqueous TiO₂ Interface

Jun Cheng,* Joost VandeVondele, and Michiel Sprik

5437

5478

dx.doi.org/10.1021/jp500288s

dx.doi.org/10.1021/jp501452g

dx.doi.org/10.1021/in500769a

Physical Processes in Nanomaterials and Nanostructures

5501

dx.doi.org/10.1021/ip409967a

Optical Properties and Quasiparticle Band Gaps of Transition-Metal Atoms Encapsulated by Silicon Cages M. I. A. Oliveira, R. Rivelino,* F. de Brito Mota, and G. K. Gueorquiev*

5510

dx.doi.org/10.1021/jp5006555

Modulating the Electronic Properties of Multimeric Thiophene Oligomers by Utilizing Carbon Nanotube Confinement Takashi Yumura* and Hiroki Yamashita

5523

dx.doi.org/10.1021/jp408126e

Direct Growth of Graphene Films on Sapphire (0001) and (1120) Surfaces by Self-Catalytic Chemical Vapor Deposition Kosuke Saito and Toshio Ogino*

5530

dx.doi.org/10.1021/jp409236t

Controlling the Electronic Properties of Nanodiamonds via Surface Chemical Functionalization: A DFT Study Noam Brown and Oded Hod*

5538

dx.doi.org/10.1021/jp410147p

Reversible Sulfidation of Pt_{0.3}Pd_{0.7} Nanoparticles Investigated by in Situ Time-Resolved XAS Jocenir Boita, Fabiano Bernardi, Marcus Vinícius Castegnaro, Lucas Nicolao, Maria C. M. Alves, and Jonder Morais*

dx.doi.org/10.1021/jp411240u

Encapsulated Water Inside Mo₁₃₂ Capsules: The Role of Long-Range Correlations of about 1 nm Miquel Garcia-Ratés, Pere Miró, Achim Müller, Carles Bo, and Josep Bonet Avalos*

5556



dx.doi.org/10.1021/jp411951h

Comparative Method To Quantify Dielectric Constant at Nanoscale Using Atomic Force Microscopy Reynier I. Revilla, Xiao-Jun Li, Yan-Lian Yang,* and Chen Wang*

5563

dx.doi.org/10.1021/ip412097d

Optical and Morphological Characterization of Tb_{0.01}Zr_{0.99}O₂/(Precursor Eu_{0.02}Y_{1.96}O₃) Core/5hell Nanoparticles as Temperature Sensors in Fast Heating Events Ray Gunawidiaia. Thandar Mvint, and Hergen Eilers*

5570

dx.doi.org/10.1021/jp412150j

Direct Measurement of Acceptor Group Localization on Donor-Acceptor Polymers Using Resonant Auger Spectroscopy Matthew Gliboff, Dana Sulas, Dennis Nordlund, Dane W. deQuilettes, Phu D. Nguyen, Gerald T. Seidler, Xiaosong Li, and David S. Ginger*

5579

dx.doi.org/10.1021/jp412228r

Structure and Dynamics of Octamethyl-POSS Nanoparticles

Niina Jalarvo, Olivier Gourdon, Georg Ehlers, Madhusudan Tyagi, Sanat K, Kumar, Kerwin D, Dobbs, Robert J, Smallev, William E. Guise, Anibal Ramirez-Cuesta, Christoph Wildgruber, and Michael K. Crawford*

5593

dx.doi.org/10.1021/jp500861n

Tunable Band Structures of Heterostructured Bilayers with Transition-Metal Dichałcogenide and MXene Monolayer Zhinan Ma, Zhenpeng Hu, Xudong Zhao, Qing Tang, Dihua Wu, Zhen Zhou,* and Lixin Zhang

5600

dx.doi.org/10.1021/jp5013126

Influence of Donor-Acceptor Arrangement on Charge Transport in Conjugated Copolymers Haihua Xu, Jun Li, Jiangquan Mai, Ting Xiao, Xinhui Lu, and Ni Zhao*

5606

dx.doi.org/10.1021/jp5013472

Critical Effect of Segmental Dynamics in Polybutadiene/Clay Nanocomposites Characterized by Solid State 1H NMR Spectroscopy

Yun Gao, Rongchun Zhang, Weifeng Lv, Qingjie Liu, Xiaoliang Wang,* Pingchuan Sun, H. Henning Winter, and Gi Xue