#### CHEMISTRY & SUSTAINABILITY

# **CHEMSUSCHEM**

### **ENERGY & MATERIALS**

10/2008



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## **COVER PICTURE**



The cover picture shows a scheme for the efficient rhodium-catalyzed evolution of  $H_2$  or  $D_2$  from formic acid (HCOOH), a substance produced naturally by ants. The use of hydrogen as an environmentally benign secondary energy resource has attracted much attention, however, high-density storage and safe transportation of gaseous hydrogen remain problematic. An approach that can contribute also to cut carbon dioxide emissions is the use of  $CO_2$  as hydrogen carrier to produce formic acid, a water-soluble liquid which is easy to store and carry. In their Full Paper on page 827 ff., S. Fukuzumi et al. describe how HCOOH is efficiently and selectively decomposed to produce  $H_2$  and  $CO_2$  in 1:1 ratio without the formation of CO in aqueous solution at 298 K catalyzed by the water-soluble rhodium aqua complex  $[Rh^{|||}(Cp^*)(bpy)(H_2O)]SO_4$ .  $H_2$  evolution occurs by formation of the hydride complex (Rh-H), which undergoes efficient H/D exchange with deuteron in  $D_2O$  to form the deuteride complex (Rh-D) in competition with the reaction with deuteron to yield  $D_2$  and  $D_2$  and  $D_2$  and  $D_3$ .

#### **NEWS**

Spotlights on our sister journals

796 - 797

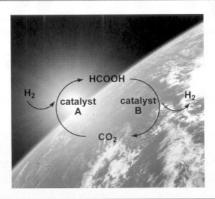


### HIGHLIGHTS

S. Enthaler\*

801 - 804

Carbon Dioxide—The Hydrogen-Storage Material of the Future?

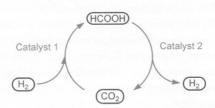


Fuelling the economy: In the search for sustainable and renewable energy systems, the hydrogen economy could be an alternative if several requirements can be fulfilled in the future. One major challenge is still the search for appropriate hydrogen-storage systems. The potential application of carbon dioxide as a hydrogen carrier is discussed in this Highlight.

F. Joó\*

805 - 808

Breakthroughs in Hydrogen Storage— Formic Acid as a Sustainable Storage Material for Hydrogen



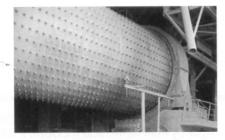
A boost for fuel cells: Recent results suggest that formic acid is a convenient hydrogen-storage material: its decomposition yields CO-free hydrogen while the co-produced carbon dioxide can be hydrogenated back to formic acid. The hydrogen generated in this way is suitable for fuel cell applications.

### **CONCEPTS**

M. Rossi,\* C. Della Pina, M. Pagliaro, R. Ciriminna, P. Forni

809 - 812

Greening the Construction Industry: Enhancing the Performance of Cements by Adding Bioglycerol



Greener building blocks: The addition of glycerol, a by-product of biodiesel manufacturing, to cement eases its grinding and handling while considerably enhancing the strength of the resulting concrete. For instance, less energy is needed to grind the so-called clinker (a calcined mixture of limestone, sand, clay, and iron ore) to the required particle size in a ball mill (see picture: photograph courtesy of Grace Construction Products).

# **COMMUNICATIONS**

X. Miao, C. Fischmeister,\* C. Bruneau, P. H. Dixneuf

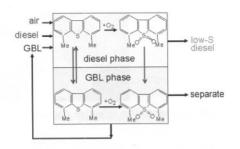
813-816

Dimethyl Carbonate: An Eco-Friendly Solvent in Ruthenium-Catalyzed Olefin Metathesis Transformations

Ru 'n' DMC: A series of ruthenium-catalyzed olefin metathesis transformations were performed in the eco-friendly solvent dimethyl carbonate (DMC), and it was demonstrated that this solvent can be used as a substitute to dichloromethane or aromatic solvents. The ethenolysis of methyl oleate using the first-generation Hoveyda catalyst was also performed in DMC, where similar conversions were observed to those in toluene (82 vs 88 %).

#### Desperately seeking desulfurization:

Organic sulfur compounds (OSCs) in transportation fuels contribute to acid rain and can deactivate catalysts in automotive applications. A new catalyst-free method to convert OSCs into sulfones in lactones by air at 140 °C and atmospheric pressure has been developed which can be used in the removal of OSCs from oil fractions or as a post-treatment to remove refractory sulfur after standard hydrodesulfurization.

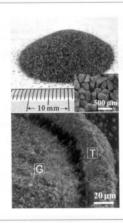


X. Xu, J. A. Moulijn, E. Ito, R. Wagemans, M. Makkee\*

817-819

Deep Desulfurization of Fossil Fuels by Air in the Absence of a Catalyst

Bucket-and-spade chemistry: An environmentally friendly and highly efficient method for growing multiwalled carbon nanotubes (T) on a large scale has been developed which uses naturally abundant resources, namely garnet sand (G) as a catalyst precursor and support, and city gas as the carbon source. The asproduced carbon nanotubes have a well-crystallized wall structure and are easily separated from the garnet sand by sonication.



M. Endo,\* K. Takeuchi, Y. A. Kim, K. C. Park, T. Ichiki, T. Hayashi, T. Fukuyo, S. Iinou, D. S. Su, M. Terrones, M. S. Dresselhaus

820 - 822

Simple Synthesis of Multiwalled Carbon Nanotubes from Natural Resources

Up the TEMPO: A novel, three-component catalyst system consisting of acetamido-TEMPO, copper bromide, and 4-pyrrolidinopyridine not only gives the highest reported turnover frequencies (up to 200 turnovers per hour) for sol-

vent-free aerobic oxidation of primary alcohols to aldehydes at ambient temperature and pressure, but also displays exceptionally high selectivity toward benzylic and allylic primary alcohols.

N. Jiang, A. J. Ragauskas\*

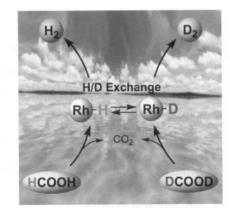
823 - 825

Copper-Catalyzed Highly Efficient Aerobic Oxidation of Alcohols under Ambient Conditions

## **FULL PAPERS**

#### Forming formate and generating gas:

The water-soluble rhodium aqua complex  $[Rh^{III}(Cp^*)(bpy)(H_2O)]^{2+}$  efficiently and selectively catalyzes the decomposition of formic acid to  $H_2$  and  $CO_2$  in aqueous solution at 298 K. Hydrogen evolution occurs through formation of the formate complex,  $[Rh^{III}(Cp^*)-\{OC(O)H\}(bpy)]^+$ , followed by a ratedetermining  $\beta$ -hydrogen elimination to afford the hydride complex,  $[Rh^{III}(Cp^*)(H)(bpy)]^+$ , the catalytic active species.



S. Fukuzumi,\* T. Kobayashi, T. Suenobu

827 - 834

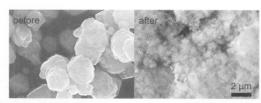
Efficient Catalytic Decomposition of Formic Acid for the Selective Generation of H<sub>2</sub> and H/D Exchange with a Water-Soluble Rhodium Complex in Aqueous Solution

# CHEMSUSCHEM

Y. K. Krisnandi, R. Eckelt, M. Schneider, A. Martin, M. Richter\*

835 - 844

Glycerol Upgrading over Zeolites by Batch-Reactor Liquid-Phase Oligomerization: Heterogeneous versus Homogeneous Reaction



Touching base: The selective conversion of glycerol to linear dimers was studied in a liquid-phase batch reaction at 260 °C under base catalysis. The reaction only marginally benefits from the use of Na/Cs-modified solid zeolites, as

the crystallinity of the zeolite is lost within the first 2-6 h of reaction (see SEM images of CsX). The alkali cations are released into the liquid, and the reaction profile becomes similar to that of a homogeneously catalyzed reaction.

A. Kamimura,\* K. Yamada, T. Kuratani, Y. Oishi, T. Watanabe, T. Yoshida, F. Tomonaga

845 - 850

DMAP as an Effective Catalyst To Accelerate the Solubilization of Waste Fiber-Reinforced Plastics











MeOH-soluble oil CHCl3-soluble solid

residues

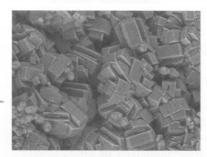
Break up, make up: Waste fiber-reinforced plastic (FRP), which is a difficult plastic in terms of monomer recycling, can be efficiently depolymerized in the presence of 4-(dimethylamino)pyridine (DMAP) in supercritical methanol. The

present method also enables separation of the FRP into its monomeric material, linker units, and inorganic ingredients such as glass fiber and filler, all ready for recycling.

S. Ivanova, E. Vanhaecke, B. Louis, S. Libs, M.-J. Ledoux, S. Rigolet, C. Marichal, C. Pham, F. Luck, C. Pham-Huu\*

851 - 857

Efficient Synthesis of Dimethyl Ether over HZSM-5 Supported on Medium-Surface-Area B-SiC Foam



Foam lends support: The performance of a supported zeolite catalyst was studied in the methanol dehydration reaction to produce dimethyl ether. The smaller size of the HZSM-5 zeolite particles supported on β-SiC foam as compared to regular HZSM-5 particles leads to better diffusion of reactant molecules in and product molecules out of the catalyst, in turn leading to superior catalyst stability and better resistance to deactivation.

Supporting information at www.chemsuschem.org (see article for access details).



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

\* Author to whom correspondence should be addressed.

# **INTERVIEW**

Nanotechnology Plays a Key Role in the Development of New Energy Systems

U. Buller ...... 858 – 859

# **BOOKS**

Hydrogen Energy · D. A. J. Rand and R. M. Dell Ionic Liquids in Synthesis · Peter Wasserscheid and Tom Welton (Eds.) Claudio Bianchini ...... 863 Ralf Ludwig ...... 863