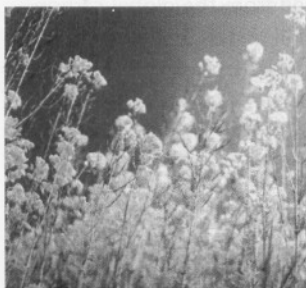


# CHEMSUSCHEM

ENERGY &amp; MATERIALS

05/2008



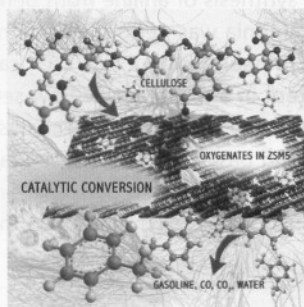
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All articles in this issue have already appeared online in Wiley InterScience. See <http://www.chemsuschem.org> under EarlyView®

## COVER PICTURE



The cover picture shows a scheme for the conversion of cellulose into gasoline-range aromatics by catalytic fast pyrolysis. Owing to its recalcitrance, there are currently no economical processes for the direct conversion of lignocellulosic biomass into useful chemicals and fuels. G. W. Huber et al. report in the Communication on page 397 ff. a process that they have developed which involves the thermal decomposition of cellulose to smaller volatile oxygenates as the first step. These biomass-derived species then enter the pores of the zeolite catalyst ZSM5, where they undergo a series of dehydration, decarbonylation, decarboxylation, isomerization, oligomerization, and dehydrogenation reactions that lead to aromatics, including naphthalene, ethylbenzene, toluene, and benzene, and by-products such as carbon monoxide, carbon dioxide, and water. All this takes place at short residence times (less than 2 min) at 600 °C in a single reactor.

## NEWS

Spotlights on our sister journals

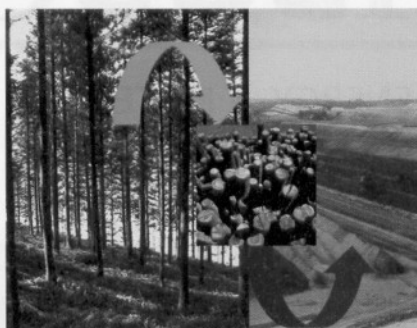
378–379

## ESSAY

F. Scholz,\* U. Hasse

381 – 384

## Permanent Wood Sequestration: The Solution to the Global Carbon Dioxide Problem



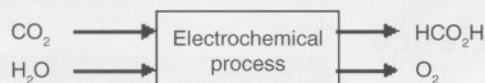
**Seeing the woods for the trees:** The global CO<sub>2</sub> problem can only be solved by the introduction of a permanent carbon sink based on the use of natural photosynthesis. In the “wood growth and burial process”, humans produce biomass, especially wood, for it to be later removed from the global carbon cycle by burial under anaerobic conditions (e.g. on the bottom of emptied open pits). Moreover, the buried wood is a deposited good and potentially available for future use.

## CONCEPT

C. Oloman,\* H. Li

385 – 391

## Electrochemical Processing of Carbon Dioxide



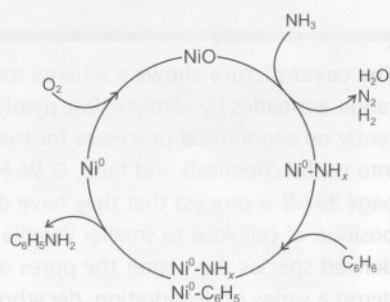
**Decreasing CO<sub>2</sub> by reduction:** Electro-reduction is an option for the conversion of CO<sub>2</sub> into useful chemicals. Experimental data from a 100-A continuous reactor have been extrapolated to the conceptual design of processes for the

conversion of CO<sub>2</sub> into formate/formic acid on a commercial scale. The costs and return on investment for a range of values of the carbon credit accrued to such an operation have also been estimated.

## COMMUNICATIONS

N. Hoffmann, E. Löffler, N. A. Breuer, M. Muhler\*

393 – 396

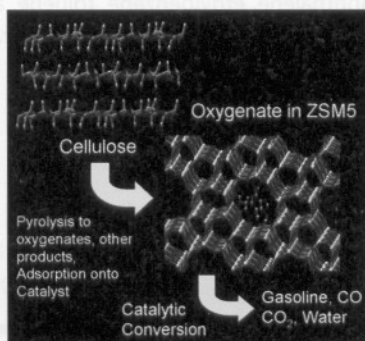
On the Nature of the Active Site for the Oxidative Amination of Benzene to Aniline over NiO/ZrO<sub>2</sub> as Cataloreactant

**Suspended amination:** Semi-batch oxidative synthesis of aniline from benzene and ammonia was performed at atmospheric pressure using a NiO/ZrO<sub>2</sub> cataloreactant in a microreactor flow setup. A Langmuir–Hinshelwood mechanism is suggested based on the surface reaction between adsorbed benzene- and ammonia-derived NH<sub>x</sub> species on metallic Ni surface sites.

T. R. Carlson, T. P. Vispute, G. W. Huber\*

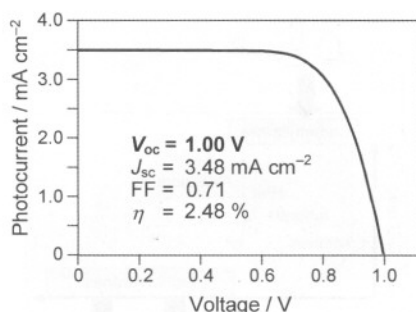
397 – 400

## Green Gasoline by Catalytic Fast Pyrolysis of Solid Biomass Derived Compounds



**A fuelling success:** High-quality aromatic fuel additives can be produced directly from solid biomass feedstocks by catalytic fast pyrolysis in a single catalytic reactor at short residence times. High heating rates and catalyst-to-feed ratios are needed to ensure that pyrolyzed biomass compounds enter the pores of the ZSM5 catalyst and that thermal decomposition is avoided. Product selectivity is a function of the active site and pore structure of the catalyst.

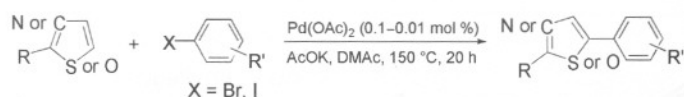
**The big 1.0:** A dye-sensitized solar cell that combines Mg-containing TiO<sub>2</sub> electrodes and an organic photosensitizer 2-cyano-3-(4-*N,N*-diphenylaminophenyl)-*trans*-acrylic acid displays the highest open-circuit voltage reported so far ( $V_{oc} = 1.00$  V). The electrodes have a negatively shifted conduction band, and the photosensitizer has a sufficiently negative LUMO energy level to inject the photoexcited electrons into the electrode efficiently.



S. Iwamoto,\* Y. Sazanami, M. Inoue, T. Inoue, T. Hoshi, K. Shigaki, M. Kaneko, A. Maenosono

401 – 403

**Fabrication of Dye-Sensitized Solar Cells with an Open-Circuit Photovoltage of 1 V**



**How low can Pd go?** The direct arylation of heteroaryl compounds under very low loadings of Pd(OAc)<sub>2</sub> as catalyst and in the absence of any added ligand proceeds in high yield. Turnover

numbers up to 10 000 are observed for the coupling of activated aryl bromides with thiazole, thiophene or furan derivatives (see scheme; DMAc = *N,N*-dimethylacetamide).

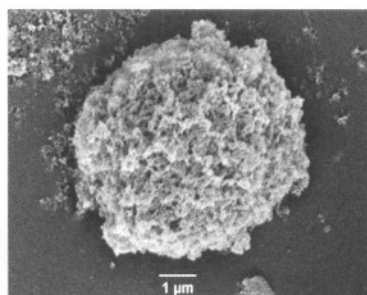
F. Požgan, J. Roger, H. Doucet\*

404 – 407

**Ligand-Free Palladium-Catalysed Direct Arylation of Heteroaromatics Using Low Catalyst Loadings**



**Holey starch!** Mesoporous materials with tuneable characteristics have been prepared from biomass-derived  $\alpha$ -D-polysaccharides by a microwave-assisted strategy. Careful selection of the preparation temperature allows control of the crystallinity, particle morphology and textural properties of the resulting materials, leading to surface areas approaching 200 m<sup>2</sup>g<sup>-1</sup> and mesopore volumes over 0.6 cm<sup>3</sup>g<sup>-1</sup>.



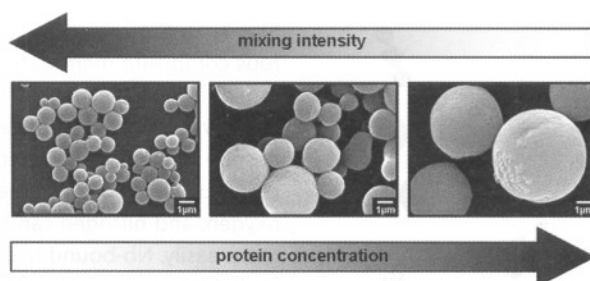
R. J. White, V. L. Budarin, J. H. Clark\*

408 – 411

**Tuneable Mesoporous Materials from  $\alpha$ -D-Polysaccharides**



## FULL PAPERS



**Along came a spider:** Spider silk proteins are well suited to create microspheres. Such silk microspheres meet the demanding requirements for the delivery of active ingredients such as

drugs and pharmaceutical proteins. Control parameters for the formation of microspheres were determined to obtain silk spheres with defined diameters and size distributions.

A. Lammel, M. Schwab, U. Slotta, G. Winter, T. Scheibel\*

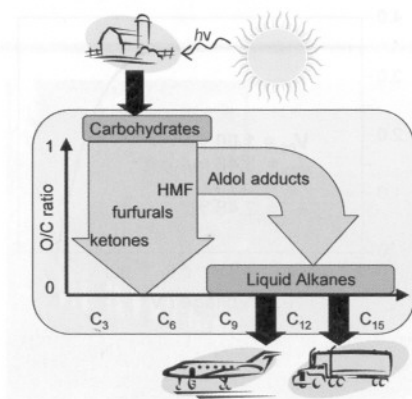
413 – 416

**Processing Conditions for the Formation of Spider Silk Microspheres**

R. M. West, Z. Y. Liu, M. Peter,  
J. A. Dumesic\*

417–424

## Liquid Alkanes with Targeted Molecular Weights from Biomass-Derived Carbohydrates

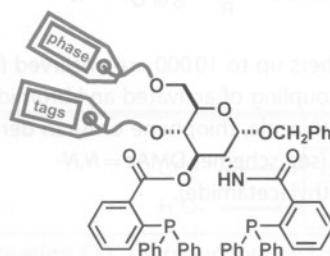


**Right on target:** Transportation fuels can be directly produced from renewable biomass resources by converting carbohydrates into alkanes with targeted molecular weights, such as  $C_8$ – $C_{15}$  for jet-fuel applications. Targeted alkanes can be produced from a variety of biomass-derived carbonyl compounds, such as fructose, 5-hydroxymethylfurfural, 5-methylfurfural, 2-furaldehyde, and acetone.

V. Benessere, A. De Roma, F. Ruffo\*

425–430

## Carbohydrates as Building Blocks of Privileged Ligands for Multiphasic Asymmetric Catalysis

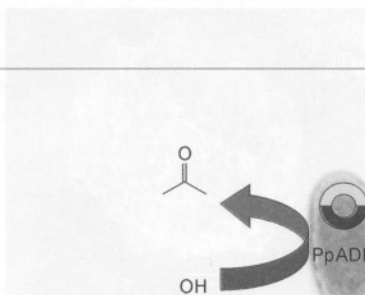


**A sweet privilege:** Aimed at combining the high chemical performance of asymmetric catalysis with the increasing need of sustainability, Trost-like ligands were prepared that contain both coordinating functions and phase tags on a D-glucose scaffold. The ligands were then applied with Pd in multiphasic homogeneous catalysis with promising results.

I. Lavandera, A. Kern, M. Schaffenberg,  
J. Gross, A. Glieder, S. de Wildeman,  
W. Kroutil\*

431–436

## An Exceptionally DMSO-Tolerant Alcohol Dehydrogenase for the Stereoselective Reduction of Ketones



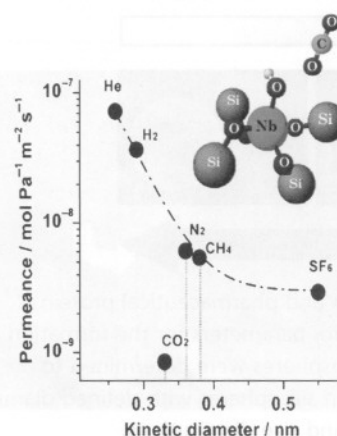
**Suffering sulfur gladly:** A novel short-chain alcohol dehydrogenase from *Paracoccus pantotrophus* (PpADH) has been identified and overexpressed in *E. coli* and then used to stereoselectively

reduce ketones. The enzyme displays an excellent tolerance towards dimethyl sulfoxide (DMSO), with high conversions observed in the presence of 50% v/v DMSO.

V. Boffa, J. E. ten Elshof,\* A. V. Petukhov,  
D. H. A. Blank

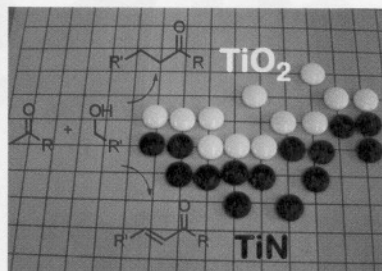
437–443

## Microporous Niobia–Silica Membrane with Very Low $CO_2$ Permeability



**Stayin' in the membrane:** A microporous composite membrane composed of niobia and silica shows an exceptionally low permeability for carbon dioxide despite its small size. Other small molecules such as hydrogen, methane, oxygen, and nitrogen can pass much more easily. Nb-bound hydroxy groups probably act as strong adsorption sites for carbon dioxide. Such a gas-selective ceramic membrane may be useful to separate  $CO_2$  from gas mixtures.

**TiN can:** As useful as palladium but 500 times less expensive, mesoporous  $\text{TiO}_2$  and TiN catalyse the alkylation of ketones with alcohols, a reaction that was previously limited to noble-metal-based catalysts (see picture). The TiN catalyst yields unsaturated compounds, while the oxide-based catalyst mainly yields saturated coupling products.



A. Fischer, P. Makowski, J.-O. Müller, M. Antonietti, A. Thomas, F. Goettmann\*

444 – 449

**High-Surface-Area  $\text{TiO}_2$  and TiN as Catalysts for the C–C Coupling of Alcohols and Ketones**

## When in Rome, do as the Romans do:

The results of a case study on Rome (Italy) show that an average citizen in one year (2002) uses directly or indirectly as much as 45 tons of abiotic materials (e.g. minerals, raw fuel, topsoil). In one year, each Roman releases 20 tons  $\text{CO}_2$ , 50 kg CO, 36 kg  $\text{NO}_x$  and 24 kg  $\text{SO}_2$ , and generates about 450 kg of solid waste.



M. Ascione,\* L. Campanella, F. Cherubini, S. Bargigli, S. Ulgiati

450 – 462

**The Material and Energy Basis of Rome: An Investigation of Direct and Indirect Resource Use through Material Flow, Energy and Footprint Methods**

Supporting information at [www.chemsuschem.org](http://www.chemsuschem.org) (see article for access details).

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

\* Author to whom correspondence should be addressed.

## INTERVIEW

“Water Splitting Could Solve Our Energy Problem”

M. Beller ..... 463 – 465

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**Organic Synthesis with Enzymes in Non-Aqueous Media** · Giacomo Carrea and Sergio Riva (Eds.)

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