

Abstracts

CATALYSIS – INDUSTRIAL PROCESS

Kilogram-Scale Asymmetric Ruthenium-Catalyzed Hydrogenation of a Tetrasubstituted Fluoroenamide

A. Stumpf, M. Reynolds, D. Sutherlin, S. Babu, E. Bappert, F. Spindler, M. Welch and J. Gaudino, *Adv. Synth. Catal.*, 2011, **353**, (18), 3367–3372

Ru-catalysed asymmetric homogeneous hydrogenation (AHH) was used as the key step of a multi-kilogram scale synthesis of an enantiomeric fluoropiperidine. The AHH of a tetrasubstituted β -fluoroenamide was carried out under mild conditions using a Ru/Josiphos catalyst with an ee of 98%.

CATALYSIS – REACTIONS

Hydrodeoxygenation of Waste Fat for Diesel Production: Study on Model Feed with Pt/Alumina Catalyst

A. T. Madsen, E. H. Ahmed, C. H. Christensen, R. Fehrmann and A. Riisager, *Fuel*, 2011, **90**, (11), 3433–3438

Hydrodeoxygenation of a model feed mixture has been investigated. Oleic acid and tripalmitin in molar ratio 1:3 were hydrotreated at 325°C with 20 bars H₂ in a stirred batch autoclave with 5 wt% Pt/ γ -Al₂O₃. Hydrogenation of both reactants was limited and decarboxylation or decarbonylation of the ester and carboxylic acid functionalities were highly favoured, giving C chain lengths of odd numbers. Pd/ γ -Al₂O₃ was found to be slightly more active than Pt/ γ -Al₂O₃ and had a higher ratio of decarboxylation and decarbonylation to hydrogenation, while Ni/ γ -Al₂O₃ was substantially less active. The conversion of oleic acid increased from 6% to 100% when the temperature was increased from 250°C to 325°C.

Selective Hydrogenation of Sunflower Oil over Noble Metal Catalysts

S. McArdle, S. Girish, J. J. Leahy and T. Curtin, *J. Mol. Catal. A: Chem.*, 2011, **351**, 179–187

Pd and Pt supported on Al₂O₃, ZrO₂ and TiO₂ were screened as heterogeneous catalysts for the selective hydrogenation of sunflower oil in a batch reactor under different operating conditions. Metal dispersions between 6–69% and loadings between 0.3–3.9% were studied for promotion of selectivity in *cis* C_{18:1}. Pd catalysts were found to be much more active than a

conventional Ni catalyst. The Pt catalyst was not as active as the Pd catalysts but produced lower *trans* fatty acids. The level of *trans* could be further reduced by increasing the operating pressure to 10 bar and reducing the reaction temperature to 100°C especially with the Pt catalyst.

The Conversion of 1,8-Cineole Sourced from Renewable Eucalyptus Oil to *p*-Cymene over a Palladium Doped γ -Al₂O₃ Catalyst

B. A. Leita, P. Gray, M. O'Shea, N. Burke, K. Chiang and D. Trimm, *Catal. Today*, 2011, **178**, (1), 98–102

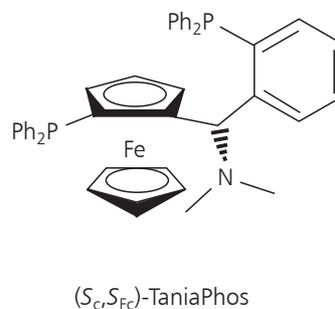
The conversion of the title 1,8-cineole over a Pd-doped γ -Al₂O₃ catalyst was studied. Both Pd and γ -Al₂O₃ were found to be bifunctional catalysts but the Pd-doped system showed very high activity and selectivity, yielding >99% *p*-cymene, while producing large amounts of H₂ at a bed temperature of ~250°C. The reaction mechanism is suggested to involve C–O bond fission in cineole, followed by dehydrogenation/isomerisation to give *p*-cymene.

Asymmetric Synthesis of 2-Alkyl-3-phosphonopropanoic Acid Derivatives via Rh-Catalyzed Asymmetric Hydrogenation

L.-B. Luo, D.-Y. Wang, X.-M. Zhou, Z. Zheng and X.-P. Hu, *Tetrahedron: Asymmetry*, 2011, **22**, (24), 2117–2123

The ferrocene-based diphosphine ligand (*S_c,S_{fc}*)-TaniaPhos was shown to be highly efficient in the Rh-catalysed asymmetric hydrogenation of 3-aryl-2-(phosphonomethyl)propenates. Excellent enantioselectivity (90–98% ee) and high catalytic activity (S/C up to 1000) were exhibited.

L.-B. Luo *et al.*, *Tetrahedron: Asymmetry*, 2011, **22**, (24), 2117–2123



α,β -Unsaturated Imines via Ru-Catalyzed Coupling of Allylic Alcohols and Amines

J. W. Rigoli, S. A. Moyer, S. D. Pearce and J. M. Schomaker, *Org. Biomol. Chem.*, 2012, **10**, (9), 1746–1749

α,β -Unsaturated imines were synthesised using only an allylic alcohol, an amine and a Ru catalyst. The use of large excesses of oxidants or dehydrating reagents and the purification of sensitive intermediates were not required. The reaction was most effective with trisubstituted allylic alcohols. The reaction conditions are mild enough to preserve other unsaturated functional groups from reduction. The ability of Milstein's PNN Ru catalyst to catalyse the efficient redox isomerisation of secondary allylic alcohols to the corresponding ketones was also demonstrated for the first time.

FUEL CELLS

Products of SO₂ Adsorption on Fuel Cell Electrocatlysts by Combination of Sulfur K-Edge XANES and Electrochemistry

O. A. Baturina, B. D. Gould, A. Korovina, Y. Garsany, R. Stroman and P. A. Northrup, *Langmuir*, 2011, **27**, (24), 14930–14939

SO₂ adsorption products on Pt/Vulcan C catalyst coated membranes (CCMs) were investigated at different electrode potentials using a combination of *in situ* S K-edge XANES spectroscopy and electrochemical techniques. SO₂ was adsorbed from a SO₂/N₂ gas mixture with the Pt/Vulcan C electrode potential held at 0.1, 0.5, 0.7 or 0.9 V *vs* RHE. S⁰ adatoms were identified as the SO₂ adsorption products at 0.1 V; mixtures of S⁰, SO₂ and sulfate/bisulfate ((bi)sulfate) ions at 0.5 and 0.7 V; and (bi)sulfate ions at 0.9 V.

Effect of Deactivation and Reactivation of Palladium Anode Catalyst on Performance of Direct Formic Acid Fuel Cell (DFAFC)

S. M. Baik, J. Han, J. Kim and Y. Kwon, *Int. J. Hydrogen Energy*, 2011, **36**, (22), 14719–14724

Pd and Pt were used as anode and cathode DFAFC catalysts, respectively, and were applied to a Nafion membrane by CCM spraying. As multiple repeated DFAFC operations were performed, the cell performance of DFAFC steadily degraded. This is attributed to the electrooxidation of Pd into Pd–OH, which occurs between 0.1 and 0.55 V. In CV experiments where the voltages applied to the DFAFC single cell are lower than 0.7 V *vs* DHE, the cell performance was further deactivated due to continuous production

of Pd–OH. Conversely, in CV experiments where the voltage was higher than 0.9 V *vs* DHE, cell performance was reactivated due to redox reactions of Pd–OH into Pd–O and Pd–O into Pd.

Development of a Catalytic Hollow Fibre Membrane Microreactor as a Microreformer Unit for Automotive Application

M. A. Rahman, F. R. García-García and K. Li, *J. Membrane Sci.*, 2012, **390–391**, 68–75

A catalytic hollow fibre membrane microreactor (CHFMMR) was prepared by electroless plating of a uniform, defect-free Pd/Ag membrane with a total thickness of 5.0 μm onto the outer layer of a YSZ hollow fibre substrate. A thin layer of a 10 wt% NiO/MgO–CeO₂ ethanol steam reforming (ESR) catalyst (max. 1.3 wt%) with a high surface area was impregnated into the YSZ hollow fibres using the sol–gel Pechini method. ESR was carried out and high purity H₂ was obtained outside the shell with a yield of <53% of the total H₂ produced in the ESR. This CHFMMR can be used in the development of on-board H₂ generation using EtOH as a fuel for PEMFCs in vehicular applications.

APPARATUS AND TECHNIQUE

Brittle Failure Analysis of PtRh₁₀ – Pt Thermocouple Wire

Y. Wang, X. Chen, G. Li, Y. Pan, X. Chen, B. Wu and J. Wang, *Precious Met. (Chin.)*, 2011, **32**, (3), 82–84

The brittle failure of PtRh₁₀–Pt thermocouples in reducing atmospheres was investigated. Electron probe microanalysis indicated that the formation of the low melting point eutectic, Pt₅Si₂, is the main cause of brittle failure.

Electrospun Carbon Nano-Felt Surface-Attached with Pd Nanoparticles for Hydrogen Sensing Application

L. Zhang, X. Wang, Y. Zhao, Z. Zhu and H. Fong, *Mater. Lett.*, 2012, **68**, 133–136

A C nano-felt with Pd NPs attached at the surface was prepared from electrospun polyacrylonitrile nano-felt surface-functionalised with amidoxime groups. The material consisted of relatively uniform and randomly overlaid C nanofibres with diameters of ~300 nm. The electrospun C nano-felt was mechanically flexible and resilient, and its resistance varied on exposure to H₂ at room temperature. This material could therefore be used for the fabrication of gas- or bio-sensors.

ELECTRICALS AND ELECTRONICS

Injection of Synthesized FePt Nanoparticles in Hole-Patterns for Bit Patterned Media

T. Hachisu, W. Sato, S. Ishizuka, A. Sugiyama, J. Mizuno and T. Osaka, *J. Magn. Magn. Mater.*, 2012, **324**, (3), 303–308

Previously, the immobilisation of FePt NPs on a thermal oxide Si substrate was carried out by utilising the Pt–S bonding between the –SH in (3-mercaptopropyl)trimethoxysilane (MPTMS) and Pt in FePt NPs. In this study, attempts were made to control the distortion of the arrangement of FePt NPs using an MPTMS layer modified with a silane coupling reaction and a geometrical structure prepared by UV nanoimprint lithography. The hole-patterns used for the geometrical structure on Si(1 0 0) were 200 nm wide, 40 nm deep, and had a 500 nm pitch. The 5.6 nm FePt NPs were used to coat the hole-patterns by using a picolitre pipette.

NANOTECHNOLOGY

Atomic Force Microscopy of the Dissolution of Cubic Pt Nanoparticle on a Carbon Substrate

N. Hoshi, M. Nakamura, C. Goto and H. Kikuchi, *J. Electroanal. Chem.*, 2012, **667**, 7–10

The dissolution mechanism of cubic Pt NPs on a C substrate in 0.1 M NaClO₄ was studied using AFM. The shape of the NPs did not change in the double layer region. The height of the NPs increased slightly at the onset potential of the oxide film formation. The NPs were dissolved from the sides in the oxide film formation region; the change of height was negligible. These results differed from those of the cubic Pt NPs on a Pt substrate, for which dissolution proceeds at the upper terrace.

PHOTOCONVERSION

Photodegradation of 2,4-D over PdO/Al₂O₃–Nd₂O₃ Photocatalysts Prepared by the Sol–Gel Method

A. Barrera, F. Tzompantzi, V. Lara and R. Gómez, *J. Photochem. Photobiol. A: Chem.*, 2012, **227**, (1), 45–50

The photocatalytic activity of 1.0 wt% PdO/Al₂O₃–Nd₂O₃ was studied in the photodegradation of 2,4-dichlorophenoxyacetic acid (2,4-D). PdO/γ-Al₂O₃ photodegraded 2,4-D; however the addition of Nd₂O₃ to γ-Al₂O₃ improves the photocatalytic activity. As the concentration of Nd₂O₃ was increased from 2 to 10 wt%, the photodegradation of 2,4-D was enhanced.

PdO/Nd₂O₃ showed scarce photocatalytic activity. 2,4-D was completely destroyed on the PdO/Al₂O₃–Nd₂O₃ photocatalysts after 6 h irradiation.

REFINING AND RECOVERY

Recovery of Platinum from Spent Catalysts by Sintering-Leaching

M. Wang, X. Dai, J. Wu, B. Zhang, Y. Wu and T. Chen, *Precious Met. (Chin.)*, 2011, **32**, (4), 6–10

The sintering-leaching method was used to treat the Al₂O₃ in spent catalysts. Pt was then recovered from the residues after the enriching process. The residual C was 0.54% with a high decoking rate of 92.66%, after roasting the spent catalysts at 600°C for 1 h. The Pt was enriched 17.87 times by the sintering-leaching process. The ‘cinder’ was mixed with NaOH and then sintered at 800°C for 2 h. The ‘clinker’ was leached at 95°C for 10 min.

SURFACE COATINGS

Room Temperature Formation, Electro-Reduction and Dissolution of Surface Oxide Layers on Sputtered Palladium Films

G. Macfie, A. Cooper and M. F. Cardosi, *Electrochim. Acta*, 2011, **56**, (24), 8394–8402

After storage under ambient conditions, peaks corresponding to sub-monolayer coverage of surface oxide and to chemisorbed O₂ were observed on linear sweep voltammograms measured on sputtered Pd films. The surface oxide films formed on the Pd were found to be relatively insoluble in neutral conditions and in the absence of Cl[–], where dissolution was limited by the solubility of Pd²⁺. In HCl the greater solubility of PdCl₄^{2–} allowed the oxide film to dissolve completely.