

Johnson Matthey Highlights

A selection of recent publications by Johnson Matthey R&D staff and collaborators

FINE CHEMICALS

Stereoselective Synthesis of the Halaven C14-C26 Fragment from D-Quinic Acid: Crystallization-Induced Diastereoselective Transformation of an α -Methyl Nitrile

F. Belanger, C. E. Chase, A. Endo, F. G. Fang, J. Li, S. R. Mathieu, A. Z. Wilcoxon and H. Zhang, *Angew. Chem. Int. Ed.*, 2015, **54**, (17), 5108

Total synthesis of the synthetic breast cancer drug Halaven involves stereocontrol of four centres and these were successfully derived from the D-quinic acid source. This allowed a crystallographic purification route in place of the chromatographic technique. It illustrates the first example of a crystallisation induced diastereoselective transformation of an α -methyl nitrile, as well as benefiting from the rigid bridged polycyclic system. The tangible benefits are an 80% reduction in cost and waste compared to the conventional route, largely due to the elimination of chromatography solvents, in accordance with green chemistry principles.

Chemists Introduce a User's Guide for Palladium Acetate

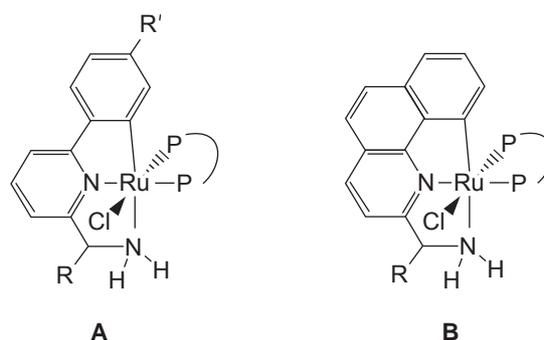
S. K. Ritter, *Chem. Eng. News*, 2016, **94**, (18), 20

Pure palladium acetate ($\text{Pd}_3(\text{CO}_2\text{CH}_3)_6$) and its two main impurities : the nitro analogue $\text{Pd}_3(\text{CO}_2\text{CH}_3)_5(\text{NO}_2)$ and polymeric $[\text{Pd}(\text{CO}_2\text{CH}_3)_2]_n$ was investigated by Process Development Engineer William A. Carole and Global R&D Manager Thomas J. Colacot (Johnson Matthey Catalysis and Chiral Technologies, USA). Various $\text{Pd}_3(\text{CO}_2\text{CH}_3)_6$ preparation processes were explored and depending on the reaction conditions, different amounts of the nitro and polymeric impurities appear. Next the team studied procedures for creating $\text{Pd}_3(\text{CO}_2\text{CH}_3)_6$ which terminate the development of impurities. The structures of $\text{Pd}_3(\text{CO}_2\text{CH}_3)_6$ and its impurities are very closely related so the purity of $\text{Pd}_3(\text{CO}_2\text{CH}_3)_6$ can be difficult to determine. The researchers used the results to create a $\text{Pd}_3(\text{CO}_2\text{CH}_3)_6$ user guide for the chemistry community. Details of the optimum synthesis of the material, how to confirm its purity and show the effect of $\text{Pd}_3(\text{CO}_2\text{CH}_3)_6$ and its impurities on catalyst performance were included in this guide.

Preparation of Pincer 4-Functionalized 2-Aminomethylbenzo[*h*]quinoline Ruthenium Catalysts for Ketone Reduction

S. Facchetti, V. Jurcik, S. Baldino, S. Giboulot, H. G. Nedden, A. Zanotti-Gerosa, A. Blackaby, R. Bryan, A. Boogaard, D. B. McLaren, E. Moya, S. Reynolds, K. S. Sandham, P. Martinuzzi and W. Baratta, *Organometallics*, 2016, **35**, (2), 277

Hydrogenation of carbonyl compounds using Ru, Rh and Ir catalysts is an increasingly attractive industrial process to produce alcohols without the use of hydrogen gas and can also eliminate other requirements for workup and removal of side products. Ru pincer complexes **A** and **B** were found to have TOF up to $6.7 \times 10^3 \text{ min}^{-1}$ and S/C < 20,000. A one-pot synthesis of the catalytic complexes using no hazardous oxidants was demonstrated. Deactivation is reduced in these complexes because of the stable orthometallated pincer structure. Further studies will extend their use into other organic transformations of interest to industry.



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NEW BUSINESSES: BATTERY TECHNOLOGIES

Porous and Hollow NiO Microspheres for High Capacity and Long-Life Anode Materials of Li-ion Batteries

S. Hao, B. Zhang, S. Ball, B. Hu, J. Wu and Y. Huang, *Mater. Des.*, 2016, **92**, 160

Anode materials for Li ion batteries were developed based on hollow NiO structures. Improved reversible capacity and improved cycling stability were found compared to a previously reported ZnO-NiO composite. Capacities $>700 \text{ mAh g}^{-1}$ at a current rate of 1 C were found and this was maintained after 400 cycles. The preparation route was straightforward and used chemical etching following ion exchange of Zn citrate template. The impressive performance is thought to be due to the unique nanostructure which allows for faster mass transport and accommodates the volume change during the cycling process.

PRECIOUS METAL PRODUCTS: NOBLE METALS

Effects of Single- and Simultaneous Triple-ion-beam Irradiation on an Oxide Dispersion-strengthened Fe12Cr Steel

V. de Castro, S. Lozano-Perez, M. Briceno, P. Trocellier, S. G. Roberts and R. Pareja, *J. Mater. Sci.*, 2015, **50**, (5), 2306

The stability of an ODS Fe12Cr after single-(Fe⁴⁺) and concurrent triple-ion-beam irradiation (Fe⁸⁺, He⁺ and H⁺) at room temperature to doses of 4.4 and 10 dpa was studied by TEM at the Joint Accelerators for Nanosciences and Nuclear Simulation (JANNUS) Saclay facility. The authors compared the results after single-ion-beam irradiation with those from a reference Fe12Cr steel produced using the same procedure. The irradiation-induced loop size and density in the ODS and reference materials were determined, and the grain boundary microchemistry and evolution of the secondary phases present were assessed. The Y-rich nanoparticles in the ODS steel are somewhat stable under these irradiation conditions despite the potential evolution of substantial Cr-rich carbides.

PROCESS TECHNOLOGIES

An Experimental Investigation of Biodiesel Steam Reforming

S. Martin, G. Kraaij, T. Ascher, D. Wails and A. Wörner, *Int. J. Hydrogen Energy*, 2015, **40**, (1), 95

Biodiesel steam reforming was investigated at different operating conditions using a precious metal based catalyst to find optimum conditions for coke-free performance, therefore circumventing catalyst deactivation. These conditions include a range of temperatures from 600°C to 800°C, pressures from 1 bar to 5 bar and the molar steam-to-carbon ratio from 3 to 5. Coke formation and sintering were found

to be the main deactivation mechanisms. The start of catalyst deactivation is determined by catalyst inlet temperature and feed mass flow per open area of catalyst. Coking can be reduced by using a precious metal catalyst at low feed flow rates ($31 \text{ g h}^{-1} \text{ cm}^{-2}$) and a high catalyst inlet temperature ($>750^\circ\text{C}$). A stable product gas composition near equilibrium attained a biodiesel conversion rate of 99% for over 100 h.

Carbon Uptake and Distribution in Spark Plasma Sintering (SPS) Processed Sm(Co, Fe, Cu, Zr)₂

A. J. Mackie, G. D. Hatton, H. G. C. Hamilton, J. S. Dean and R. Goodall, *Mater. Lett.*, 2016, **171**, 14

The C uptake in permanent magnet Sm alloys processed using SPS as an alternative to other powder processing techniques was analysed by EPMA. Higher levels of C were found in the surface down to 10 μm with some C also found within the body of the sample. This C originates from the graphite dies and was used to process the powders. It is not thought to affect the magnetic properties of the Sm based alloys as the levels are very low. However the C content may affect other materials processed using the same technique, such as spinels and glass ceramics which can have reduced transparency. C removal from the surface is recommended before heat treatment at high temperatures to prevent potential C migration into the body of the material.

The Effect of Mg Location on Co-Mg-Ru/ γ -Al₂O₃ Fischer-Tropsch Catalysts

J. R. Gallagher, P. Boldrin, G. B. Combes, D. Ozkaya, D. I. Enache, P. R. Ellis, G. Kelly, J. B. Claridge and M. J. Rosseinsky, *Phil. Trans. Roy. Soc. A, Math., Phys. Eng. Sci.*, 2016, **374**, 20150087

Fischer-Tropsch catalysts for the conversion of coal, gas or biomass to clean liquid fuels are based on Co with metal oxides, pgms and a Mg promoter. In this study, the catalyst was Co-Ru/Al₂O₃ with Mg as a structural promoter and the effect of order of addition of this metal to the support was found to have an effect on the activity, particle size and stability of the Co based catalyst. Incorporation of Mg into the Al₂O₃ phase increases the stability and activity at high temperature. However the inclusion of Mg with the Co phase significantly reduces its performance. High resolution TEM studies were used to confirm the location of the Mg after various impregnation strategies.

Importance of Surface Carbide Formation on the Activity and Selectivity of Pd Surfaces in the Selective Hydrogenation of Acetylene

B. Yang, R. Burch, C. Hardacre, P. Hu and P. Hughes, *Surf. Sci.*, 2016, **646**, 45

Density functional calculations on Pd nanoparticle catalysts for the selective hydrogenation of acetylene demonstrate that Pd(100) carbide should give higher

activity and selectivity than Pd(111) carbide. In contrast, pure Pd(111) would be expected to give higher activity and ethylene selectivity than pure Pd(100). Therefore, to explain recent experimental results reported elsewhere, the authors conclude that the catalyst surface is most likely in the carbide form under the experimental reaction conditions. The Pd(100) hydride surface was also found to be less stable than the Pd(111) hydride surface, also in accordance with published experimental results.