FROM THE LITERATURE

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Three books will soon appear for CRC Press, Taylor and Francis Group, authored specified as follows: (a) T. Cecchi (ITIS Montani, Fermo, Italy, "*Ion Pairing Chromatography*"), (b) G. Sartori and R. Maggi (Università di Parma, "*Advances in Friedel–Crafts Acylation Reactions*"), and (c) G. Floris and B. Mondovi (Università di Cagliari and Università di Roma "La Sapienza", "*Copper Amine Oxidases*").

The November 2008 issue of *Acc. Chem. Res.*, containing the Guest Editorial by Professor S.L. Buchwald of Massachusetts Institute of Technology, is dedicated to cross–coupling reactions. Within this special issue, a review–article has appeared on catalytic sequential reactions involving palladacycle–directed aryl coupling steps, as for a contribution from the Università di Parma by M. Catellani *et al.*, *loc. cit.*, 2008, **41**, 1512. The methodology used by this research group consists of the cooperative action of the palladium centre and norbornene to achieve selective aryl–aryl coupling through C–halide and C–H activation. The metal–catalyzed reaction sequence is initiated by the oxidative addition of an aryl halide to palladium(0) to form a palladium(II)–aryl bond. A review–article (P. Barbaro *et al.*, *Chem. Rev.*, 2009, **109**, 515) has reported on catalyst recovery and recycle through ion–exchange on resins. This contribution from the CNR Istituto di Chimica dei Composti Organometallici, Sesto Fiorentino, Firenze, describes the methods of catalyst immobilization and the applications to carbonylation, hydroformylation, hydrogenation – including the asymmetric version –, to oxidations and polymerization.

The Chemical Technology Section of *Dalton Trans*. (*Chem. Technol.*, 2009, **6**, T49) summarizes some new findings recently obtained at Istituto per la Scienza e la Tecnologia, Faenza, Italy: porous hydroxyapatite was synthesized over the carbon template obtained by heating wood in order to decompose the organic part of it and produce the carbon template characterized by an anisotropic pore structure, followed by calcium permeation leading to calcium carbide, and oxidation to calcium oxide further converted to calcium carbonate, and to hydroxyapatite through a phosphatization process (A. Tampieri *et al.*, *J. Mater. Chem.*, 2009, **19**, 4973). Applications of these findings for tissue repairing are predicted.

A paper from the Università di Salerno (A. Poater *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 9000) has contributed to the understanding of the role of a carbonyl group in *trans* position to a ruthenium–methylidene bond in a prototype olefin metathesis catalyst. The effect of coordinated CO is to reduce the back–donation to the methylidene group.

A review–article is devoted to catalytic oxidations in supercritical carbon dioxide, as for a contribution from the ETH Zürich (T. Seki *et al.*, *Chem. Rev*., 2009, **109**, 2409). Refs. 37–42, 72 and 94 correspond to work in this area carried out by a research group operating at the Università di Padova, the senior authors being S. Campestrini, M. Pagliaro and U. Tonellato [(a) S. Campestrini *et al.*, *J. Mol. Catal.*, 2000, **164**, 263; (b) S. Campestrini *et al.*, *Adv. Synth. Catal.*, 2001, **343**, 819; (c) R. Ciriminna *et al.*, *ibidem*, 2003, **345**, 1261; (d) R. Ciriminna *et al.*, *ibidem*, 2004, **346**, 231; (e) S. Campestrini *et al.*, *ibidem*, 2005, **347**, 825; (f) R. Ciriminna *et al.*, *Adv. Funct. Mater.*, 2005, **15**, 846; (g) R. Ciriminna *et al.*, *Org. Biomol. Chem.*, 2006, **4**, 2637; (h) R. Ciriminna *et al.*, *Chem. Eur. J.*, 2006, **12**, 5220]. The aerobic oxidation of benzyl alcohol in supercritical CO_2 was carried out at 75 °C and 21 MPa for 11 h, in the presence of tetrapropylammonium perruthenate [(c)]. A high activity was obtained by encapsulating the catalyst in modified silica [(c)]. A mechanistic study carried out by using ruthenium supported on a silica–containing matrix suggests that RuO_4^- is the catalytically active species, dioxygen operating by dehydrogenation of the ruthenium–coordinated alcohol. The activity increased by ageing the catalyst for several months [(f)]. Also silica–based supports modified with fluoro–alkyl groups were prepared [(d)]. Another catalyst was obtained by doping, with ruthenium, a hybrid fluorinated silica, a sol–gel methodology allowing the addition of $Si(OMe)_4/CF_3(CH_2)_2Si(OMe)_3$ to a solution of the ruthenium–containing compound: several benzyl– and aliphatic alcohols were oxidized to the corresponding carbonyl compounds. Furthermore, this research group reported [(h)] the preparation of lamellar silica–supported ionic liquids doped with ruthenium, leading to oxidation of alcohols to the corresponding carbonyl derivatives, with a substantially 100% selectivity.

The bis(triphenylphosphano)iminium cation, $[N(PPh_3)_2]^+$, PPN^+, has frequently been used for the isolation of organometallic anions. It has now been reported (V.J. Sussman *et al.*, *Chem. Commun.*, **2008**, 5642) that in an attempted isolation of tris(η-naphthalene)tantalate(–I) as the bis(triphenylphosphano)iminium cation (PPN^+) derivative, a product arising from the orthometallation of two phenyl rings has been isolated and structurally characterized. It is interesting to note that in the course of using [PPN]Cl for the isolation of the anionic hexacarbonyl derivatives of Group 5 of formula $[M(CO)_6]^-$, no metalation was observed (F. Calderazzo *et al.*, *Inorg. Chem*., 1983, **22**, 1865).

The preparation and catalytic performance of magnetic silica–coated palladium nanoparticles has been reported, as a contribution from the Universidade de São Paulo (L.M. Rossi *et al*., *Inorg. Chem*., 2009, **48,** 4640). The magnetic properties of the system thus obtained allowed the efficient isolation of the catalyst with an external magnetic field. The catalysts thus prepared were used in the hydrogenation of cyclohexene in the absence of any solvent. The preparation of the catalyst, reported in an earlier paper (M.J. Jacinto *et al*., *Appl. Catal. A*: *General*, 2008, **338**, 52), consists of rhodium nanoparticles immobilized on silica–coated magnetic nanoparticles: this catalytic system can be reused for about 20 times.

A contribution from the Universidad de Madrid, in collaboration with the Universidad de Barcelona and the Università di Milano (F.

Gándara *et al.*, *Inorg. Chem.*, 2009, **48**, 4707) has reported the preparation and crystal structure of three polymorphs of the lanthanum(III) complex obtained with the conjugate base of 4,4’–hexafluoro–*iso*–propylidene–bis(benzoic acid). The central metal atom is nine–coordinated, the resulting chains being linked by bridging oxygen atoms.

Coordination polynuclear complexes (S. Contaldi *et al.*, *Dalton Trans.*, **2009**, 4928) have been reported as a contribution from three Italian universities in collaboration with the Instituto Superior Técnico of Lisbon. The new pyrazolato (pz) copper–containing systems have been studied by X–ray diffraction: the acrylato– and methacrylato derivatives have the $[Cu_3(\mu_3\text{–}OH)(\mu\text{–}pz)_3]^{2+}$ unit in common. These copper(II) derivatives catalyze the oxidation of cyclohexane and cyclopentane to ketones and alcohols.

A series of papers have addressed the problem of metal oxide surfaces and their properties. Research groups operating at the Universities of Parma, Catania and Bologna (E. Biavardi *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 7447) have reported a Si(000) surface featuring molecular recognition properties through covalent functionalization with a tetraphosphonato cavitand. Scanning tunnelling microscopy (STM) and Density Functional Theory (DFT) calculations were used to study the formation of H_2O on a Rh(110) surface (C. Africh *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 3253), as for a contribution of the Università di Trieste in collaboration with the Laboratorio CNR–INFM in Basovizza and with the Universität Wien. Fast STM measurements support the combelike propagation mechanism for the reaction front. Mesoporous silicas SBA–15 and MCM–41 have been functionalized with Gd(III), the latter as its DOTA (1,4,7,10–tetraazacyclodecane– N,N’,N”,N’”–tetraacetic acid) derivative (F. Carniato *et al.*, *Chem. Commun.*, **2009**, 1246) in a contribution from the Università del Piemonte Orientale in collaboration with the Università di Torino. A paper resulting from the collaboration of the Università di Torino with the ESRF of Grenoble and the Synchrotron SOLEIL facilities at Gif–sur–Yvette describes the successful efforts aimed at shifting the light absorption of Engelhardt titanosilicalite (ETS–10) down to the visible ragion by introducing Ag^+ cations. A contribution (P. Falcaro *et al.*, *Chem. Mater.*, 2009, **21**, 2055) resulting from the collaboration of several European institutions located in Venezia, Sassari, Genova, Cagliari, Graz and Basovizza describes the formation of porous silica films characterized by a ultra–low refractive index. Along similar lines, large–pore ethane–bridged periodic mesoporous silicas functionalized with carboxylic groups have been reported (S. Fiorilli *et al.*, *Chem. Commun.*, **2009**, 4402) as a contribution from two departments of the Università di Torino. A paper contributed by the Università di Padova in collaboration with the Eindhoven University of Technology (S. Lovat *et al.*, *Inorg. Chem.*, 2009, **48**, 4724) reports that a polynuclear silsesquioxane of vanadium(V) catalyzes the cumylhydroperoxide–promoted oxidation of sulfides to sulfoxides and of amines to the corresponding *N*–oxides. A communication (G. De Luca *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 6920) contributed by the Università di Messina and the Università di Bologna reports on the self–organization of porphyrin–H and porphyrin–J on synthetic cryosotite $[Mg_3Si_2O_5(OH)_4]$ by ionic self–assembly. A contribution from two research institutions of CNR located in Bologna and Perugia, and from the Università di Perugia in collaboration with the British Museum (G. Accorsi *et al.*, *Chem. Commun.*, **2009**, 3392) has reported on the exceptional near–IR luminescence properties of cuprorivaite of formula $CaCuSi_4O_{10}$ (known as the Egyptian Blue). This material can be synthesized by heating $CaCO_3$ at 850–1000 °C with malachite $[CuCO_3\cdot Cu(OH)_2]$ in the presence of silica sand and NaOH (or KOH), the latter generated by calcining vegetable materials.

Surfaces of TiO_2 have been used for their photocatalytic properties. A paper contributed by the Universities of Milano–Bicocca, Milano, Cagliari and Venezia (R. Scotti *et al.*, *Chem. Mater.*, 2008, **20**, 4051) has reported the preparation of TiO_2 by hydrolysis of $TiCl_4$ in the presence of a polyether triblock copolymer. By calcination, mesoporous and nanocrystalline TiO_2 was obtained, as characterized by conventional surface techniques (TEM, HRTEM, XRD, area measurements). A patent assigned to Italcementi SpA, Bergamo, Italy (inventors: L. Cassar and C. Pepe, US Patent No. 6, 117, 229; Sept. 12th 2000) describes the formation of a cement characterized by a high capacity of reflecting sunlight with a minimum degree of absorption. The preferred photocatalyst is titanium dioxide, usually as its anatase modification.

A paper resulting from the collaboration of the Max–Planck–Institut (Polymerforschung in Mainz and Colloids and Interfases, Golm, Germany) with the National Center for Nanoscience and Technology, Beijing, China, has appeared (J. Zhang *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 11296) reporting that the cyclotrimer of 9,10–phenanthrenequinone is a catalyst for the exothermic oxidative dehydrogenation of ethylbenzene to styrene.

A paper contributed by the Università della Calabria (E. Di Santo *et al.*, *Organometallics*, 2009, **28**, 3716) discusses the activation of the methane C–H bond by Th^+ and U^+ in the gas phase. Through a density functional theory approach the monovalent uranium cation was found to be inert to CH_4; on the contrary, the $Th^+ + CH_4$ exothermic (43 kJxmol^{-1}) dehydrogenation proceeds from the initial $[Th\cdot CH_4]^+$ adduct.

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