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► **To cite this version:**

Jean-Cyrille Hierso, Yasuhiro Uozumi. Cluster Preface: Heterogeneous Catalysis. SYNLETT, 2016, 27 (08), pp.1177 - 1178. 10.1055/s-0035-1562061 . hal-04563419

HAL Id: hal-04563419

<https://hal.science/hal-04563419>

Submitted on 2 May 2024

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Cluster Preface: Heterogeneous Catalysis

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Jean-Cyrille Hierso is full professor of Chemistry since 2009, heading the group of 'Organometallic Chemistry and Catalysis' at the Institute of Molecular Chemistry at the University of Bourgogne Franche-Comté (UBFC). He has interest in the fields of organometallic chemistry, ligand design, homo- and heterogeneous catalysis, chemical physics, and material sciences. In 2011 he was awarded the National Prize for Coordination Chemistry from the French Chemical Society (SCF), and at the end of 2012 he was elected a junior Member of the French Professors Academy 'Institut Universitaire de France' (IUF).

Yasuhiro Uozumi is a full professor at the Institute for Molecular Science (IMS) in Okazaki, Japan since 2000, and has also been appointed as a research team leader at RIKEN in Wako, Japan. He is interested in the fields of organic synthesis, organometallic chemistry, transition metal catalysis, and green chemistry. He was awarded The Chemical Society of Japan (CSJ) Award for Creative Work (2007), the Ministerial Award for Green Sustainable Chemistry (2007), the Inoue Prize (2010), and The Ministerial Commendation for Science and Technology (2014).

Keywords: sustainable chemistry, nanocatalysts, organocatalysts, gold, palladium, nanoparticles, peptides, polymer-supports, inorganic-supports, nanotubes, epoxidation, esterification, cross-coupling, C–H functionalization, oxidation, (hetero)arenes, kinetics, supramolecular assembly, recovering, recycling.

The History of Humanity is intimately bonded to progress in Science. The Industrial Revolution of the 18th and early 19th century also profoundly changed the scientific approach, and the globalization movement that started in the second half of the 20th century also initiated mutual pooling of knowledge that *inter alia* established quantum mechanics theory,

led to walking on the moon, and other spatial exploration previously inconceivable, despite Jules Verne's vision!^[1]

Chemistry was (and still is) a central science in this progress (*synthesis, materials, energy*). Given the breakthroughs made in the three last centuries, and also the intensification of resource and energy consumption, it is reasonable to ask whether our 21th century should not shift radically to focus on how to better utilize and recycle our resources so that future generations can benefit from the remarkable advances achieved so far.

Catalytic processes fully comply with this concept, and the present *Synlett Cluster Issue* devoted to “**Heterogeneous and Immobilized Catalysts**” adds a step forward to the practical and conceptual development of recoverable catalysts. Currently, metal catalysis is the essential technology for transforming the chemical structure of matter on a large scale. Process catalysts represent dozens of billion dollars-per-year businesses worldwide only for petroleum derivatives, current chemicals and pharmaceuticals, synthetic rubber and plastics. Heterogeneous catalysts are the most applied catalysts at an industrial level (approximately 80% of all catalytic processes).

The present *Synlett Cluster Issue* covers advances in three topical fields of heterogeneous catalysis: *i*) supported organocatalysts –both chiral and achiral– (Kudo and Toy groups), *ii*) innovative cross-couplings promoted by synthetically efficient immobilized transition metals (iridium) and nanoparticles (palladium)– both from a synthetic aspect (Ohtaka, Uozumi, Sawamura and Hierso groups), and from a fundamental approach (Fairlamb group)–, *iii*) gold chemistry from nanocatalysts in inorganic and organic methodologies (Okumura, Najera and Doris groups).

More specifically, Ma and Toy report that bifunctional linear polystyrene bearing both 4-dimethylaminopyridine and a proximate tertiary amine functional group can promote

esterification reactions between an alcohol and an acid anhydride (or an acid chloride) with a recycling capacity over fifteen runs, and obviating the need for the ester products to be purified by chromatography. The Kudo group successfully inverted the stereoselectivity traditionally obtained in asymmetric epoxidation of enones (Juliá-Colonna product) by using a resin-supported peptide catalyst with an *N*-terminal primary amino group, thus allowing access to a number of difficult to synthesize enantiomers.

Another highly topical thematic treated in this *Synlett Cluster issue* is the synthesis, stabilization and understanding of palladium-based nanocatalysts applied to organic synthesis. Cross-coupling reactions and C–C bond formation form a useful synthetic toolbox in industrial processes and academic research for generating molecular materials, pharmaceuticals, and agrochemicals, as well as for endeavors in total synthesis, multicomponent reactions, fundamental knowledge in catalysis, and *etc.* Such catalytic processes were originally developed and refined under classical homogeneous conditions, and the search for their implementation in recoverable systems has followed many different paths. Ohtaka and co-workers reported the Hiyama cross-coupling (*Pd-catalyzed arenes arylation using organosilanes as the nucleophile*) without the assistance of often used fluoride additives and promoted by recyclable palladium oxide nanoparticles supported on polystyrene. Zinovyeva and Roger generated palladium-polypyrrole nanocomposites with remarkable high palladium content and used them as the first heterogeneous catalysts for substituted-pyrroles and imidazoles coupling by C–H arylation with demanding bromoarenes. The Fairlamb group in a kinetic comparative study highlighted the similarity of initial reaction rates from so-called molecular pre-catalyst and various forms of heterogeneous palladium nanocatalysts, an encouraging step toward bridging homogeneous and heterogeneous systems. Beside palladium catalysis, the highly topical theme of C–H activation/functionalization was addressed by Sawamura group for *sp*³C–H borylation of alkyl side chains of 1,3-azoles with

an iridium catalyst immobilized on a well-defined commercially available silica-supported monophosphine. The efficiency and selectivity of the immobilized catalyst is remarkable in comparison with standard homogeneous systems tested, and useful γ -boronate-2-alkyl-benzoxazole, -thiazole and -benzimidazoles were produced.

While the synthetic utility of palladium and iridium is established by several industrial processes, other transition metals are now being intensively examined. The recent renewal of interest in gold chemistry was shared between the synthesis and applications of its colloids and nanocrystals, and a reactivity which encompasses non-exhaustively oxidation and hydrogenation reactions, as well as C–C and C–heteroatom bond formation, cyclization, *etc.* The “golden part” of this *Synlett Cluster issue* is focused on varied synthesis of supported gold nanoparticles and their applications. Okumura reports a simple physical mixing between a gold metallorganic complex and inorganic supports followed by thermal treatment for gold reduction that provides a 4 nm gold(0) nanoparticles dispersed composite-material that selectively oxidizes benzyl alcohol to benzaldehyde under air. Gholinejad and Najera used polyacrylamide containing phosphinite to support highly dispersed 4 nm gold(0) nanoparticles the resulting recoverable material was used efficiently in three component condensation reaction towards propargylamines, and that has been recycle seven times. Gravel, Namboothiri, and Doris provided a contextualized concise account of the building and application of gold nanoparticles supported on carbon nanotubes: highly dispersed confined 3 nm nanoparticles promote a variety of catalytic reactions involving reduction, oxidation, formylation and deoxygenation of valuable industrial organics with gold at low loading ranging in 0.001-0.4 mol%.

Thus, this Cluster of catalytic research vividly exemplifies the creativity and diversity of the field currently devoted to “**Heterogeneous and Immobilized Catalysts**”. At the same time it points out at these roads towards better use and recycling of our resources so that our

descendants can benefit from the remarkable advances of Chemical Sciences. There is little doubt that this field will experience in the coming years further unique and/or off-trail heterogeneous approaches to catalytic organic transformations, involving immobilized ligands, nanoparticles, MOFs, dendrimers, and unusual solvents, as well as synthetic progress in challenging organic transformations, in catalyst recycling, and in catalytic systems characterization and understanding. Dear colleagues, please enjoy your reading!

Faithfully yours.

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^[1] *From the Earth to the Moon, Jules Verne, 1865.*