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Editorial

# Supported Molecular Catalysts

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This Editorial presents the Special Issue on Supported Molecular Catalysts as a forum to discuss recent advances in the immobilization and heterogenization of molecular catalysts. The scope ranges from organic synthesis and highly selective reactions through to photocatalysis and electrocatalysis, including advances in enzyme immobilization methodology. The outcome is a wide spectrum of papers encompassing all the old formal domains of catalysis research of both primary and secondary research.

Looking over this project that started early in 2017, when we sent out the invitations to contribute to this Special Issue on **Supported Molecular Catalysts**, till now at publication in April 2018, we are so impressed with this contribution to the art of heterogenization of molecular catalysts.

The Special Issue was launched to provide a forum to discuss the recent advances in immobilization of molecular catalysts and to continue the discussion as to whether we can really bring the excellent selectivity and activity of molecular catalysis to the heterogeneous realm. The specified scope was very broad: ranging from organic synthesis and highly selective reactions through photocatalysis and electrocatalysis, including advances in immobilization methodology. The outcome is a wide spectrum of papers of both primary and secondary research co-authored by reputed catalysis giants, as well as from rapidly emerging scholars of international standing.

The issue includes articles co-authored by scientists based in 19 different countries in Europe, Asia and North America testifying not only to the known international authorship of *ChemCatChem*, but to the global interest in the topic of this themed issue.

The broad scope is further reflected in the different articles included in the issue, which includes **Freire's** thorough Review of electrocatalysts based on polyoxometalates and metal-organic frameworks for energy-related reactions; the **Pagliaro and Béland** teams' insight on the broad catalytic scope of sol-gel entrapped nitroxyl radicals suitable even for cellulose nanofiber preparation; and the Review by **Artz** of covalent triazine-based frameworks as supports for both molecular as well as nanoscale catalytic species.

**Hutchings** and collaborators investigate atomically dispersed Au/C catalyst evolution before reaction in homocoupling of phenylboronic acid; a topic related to the study of **Carabineiro** and co-workers on commercial gold(I) and gold(III) compounds supported on activated carbon, multi-walled carbon nanotubes and carbon xerogel, affording leach-proof and recyclable catalysts for the aerobic and selective oxidation of cyclohexane and alcohols under mild conditions.

In a Review dedicated to Prof. Gerhard Ertl on the occasion of his 80th birthday, **Somorjai** and co-workers elucidate the origins of enhanced activity and selectivity of supported molecular catalysts. Using examples which include reactions at oxide-metal interfaces and alcohol oxidation reactions at solid–gas and solid–liquid interfaces, the team describe new insights into catalysis at the nanoparticle-support interfaces, which are catalytic environments unique to supported molecular catalysts.

**Fukuzumi** and co-workers review the strategy of immobilizing organic and inorganic molecular catalysts on solid supports for enhanced thermal and photoinduced redox reactions prohibiting, for example, bimolecular deactivation. **Basset's** team at KAUST sheds light on the hydro-metathesis reaction of 1-decene via well-defined silica-supported W, Mo, Ta carbene/carbyne complexes. The team of **Kaliaguine** at Laval Université describes the efficient glycerol acetalization over supported heteropolyacid catalysts.

**Ananikov** and co-workers at Russian Academy of Sciences describe a surprisingly rapid 'mix-and-stir' preparation of a well-defined Pd/C catalyst for efficient practical use in C–C cross coupling reactions. **Farha's** team describes a leach-proof and active and stable vanadium-oxide catalyst supported on highly porous Zr-based metal-organic framework investigated in the oxidation of 4-methoxybenzyl alcohol under an $O_2$ atmosphere.

**Buchmeiser** and co-workers demonstrate that molybdenum alkylidyne supported on dehydroxylated and end-capped silica

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has substantially higher alkyne metathesis activity than the homogeneous analogue thanks to site isolation and reduced bimolecular decomposition. A similar lack of diffusion limitations in the solid catalyst is shown by **Canivet's** team in France who describe two bipyridine-based porous polymers and their use as platforms for the heterogenization of pentamethylcyclopentadienyl rhodium catalytic species, used in the transfer hydrogenation of $\alpha$-aryl ketones.

**Karimi's** team in Iran show how perruthenate ions supported inside the channels of periodic mesoporous organosilica with a bridged imidazolium ionic liquid framework is an efficient, durable, and recoverable catalyst for the oxidative dehydrogenation of various types of amines such as benzylic, aliphatic, and cyclic aliphatic amines under mild reaction conditions.

**Mario Pagliaro** has led a research group focusing on nanochemistry, sustainability and the bioeconomy based in Sicily at Italy's CNR between late 2000 and early 2018. He ranks amongst Italy's most cited scientists in nanotechnology and materials chemistry. In recognition of his "significant contributions to the chemical sciences" in 2014 he was designated Fellow of the Royal Society of Chemistry. The achievements of his group include the organization in Sicily of 13 international meetings, from FIGIPAS 2009 through 6 editions each of the FineCat Symposium on catalysis for fine chemicals, as well as of the SuNEC conference on solar energy. Dr Pagliaro sits in the international advisory board of Chemical Society Reviews, as well as in the editorial and advisory boards of several other prestigious scientific journals. He regularly evaluates research projects for national and international research agencies, co-mentors MSci and PhD students, and has been appointed in numerous evaluation committees of Professor and PhD candidates.

**Bert Sels**, currently full professor at the KU Leuven, obtained his Ph.D. in 2000 in the field of heterogeneous oxidation catalysis. He was awarded the DSM Chemistry Award in 2000, the Incentive Award by the Societe Chimique Belge in 2005, and the Green Chemistry Award in 2015. He is currently director of the Center for Surface Chemistry and Catalysis, designing heterogeneous catalysts for future challenges in industrial organic and environmental catalysis. His expertise includes heterogeneous catalysis in biorefineries and the spectroscopic and kinetic study of active sites for small-molecule activation. He is co-chair of the Catalysis Commission of the International Zeolite Association (IZA) and co-founder of European Research Institute of Catalysis (ERIC). He is also member of the European Academy of Sciences and Arts, board member of the international advisory board of *ChemSusChem* (Wiley).

**Xiao** and co-workers in China report the discovery that porous organic polymers obtained from Tröger's Base are both efficient CO$_2$ adsorbents (which give high CO$_2$ adsorption capacities of 60 and 44 mg CO$_2$ g$^{-1}$ at 298 K for different materials under a CO$_2$ pressure of 1 bar) and highly active and stable heterogeneous catalysts in Knoevenagel reaction.

**Anwander** in Germany and Le Roux in Norway demonstrate that silica-grafted neodymium catalysts obtained by grafting methylaluminate Nd(AlMe$_4$)$_3$ onto high-surface silica materials including periodic mesoporous silicas MCM-41, SBA-15, and KIT-6 allow for the fabrication of polyisoprenes with ultrahigh molecular weight (as high as $3\times10^6$ g mol$^{-1}$) and low polydispersity, with microstructures with 99% *cis*-stereospecificity.

**Peris and Ruiz-Botella** show how two pyrene-tagged N-heterocyclic carbene complexes of rhodium(I) supported onto reduced graphene oxide afford catalytic materials suitable for the 1,4-addition of phenylboronic acid to cyclohex-2-one, and for the hydrosilylation of terminal alkynes, with the performance of the dimetallic complex better than the monometallic species.

Reporting the outcomes of a computational analysis of the redox properties of graphene-supported Ru-porphyrins as catalytic materials for electrochemical CO$_2$ reduction, **Szyja** in Poland along with co-workers in the Netherlands and in Germany show how such catalytic ensembles can efficiently activate both CO$_2$ and CH$_4$ molecules.

Using five different nanostructured carbon materials (nanodiamonds, graphene nanoplatelets, graphene oxide, reduced graphene oxide and nanohorns) to support a C-scorpionate iron(II) complex, **Martins** and co-workers in Portugal and in the Netherlands were able to produce active, selective and recyclable catalysts for alkane and alcohol oxidations, suitable for the formation of ketone-alcohol (KA) oil (cyclohexanol and cyclohexanone mixture, yields up to 29%) from microwave-assisted oxidation of cyclohexane, as well as to effectively catalyze the microwave-induced oxidation of 1- and 2-phenylethanol to acetophenone and 2-phenylacetaldehyde for seven consecutive cycles without losing catalytic activity.

**Rose** and co-workers in Germany and in California describe the first metal-free heterogeneously catalyzed hydrogenation of an alkene (diethyl benzylidenemalonate) using a catalyst consisting of a solid polyamine organic framework and molecular tris(pentafluorophenyl). They further prove that the successful hydrogen activation is due to the semi-solid frustrated Lewis pair.

The teams of **Sun and Arai**, in China and in Japan, respectively, report that the zwitterionic imidazole-urea derivative frameworks bridged by a hybrid mesoporous silica material that contains iodine and is protonated by an inorganic acid is an highly efficient heterogeneous catalyst for CO$_2$ conversion into cyclic carbonates (by reaction with epoxides) with good recyclability, offering a low-cost alternative to conventional supported transition-metal catalysts.

**Wu's** group in China reports a series of binaphthyl-osmium nanoparticles (OsNPs) with chiral modifiers which, applied to the heterogeneous asymmetric dihydroxylation of alkenes, afford the desired enantioselective dihydroxylation of alkenes with a remarkable size effect of the OsNPs, depending on the density of the covalent organic shells.

**Liu's** team in Shanghai demonstrates how an amphiphilic hyperbranched polyethoxysiloxane used as a support for the construction of bifunctional heterogeneous catalysts enables a highly efficient and recyclable catalytic system thanks to its amphiphilic nature, as well as to the well-defined dual single-site active centers distributed uniformly within monodisperse mesoporous silica nanoparticles. The team demonstrated the full practical feasibility of the one-pot preparation of optically pure biaryl alcohols in high yields and up to 99% enantioselectivity via the enantioselective tandem reaction of Pd-catalyzed Suzuki cross-coupling and Ru-catalyzed asymmetric transfer hydrogenation over supported Pd/phosphine and chiral Ru/diamine catalytic species.

The topic of silica-supported molecular catalysts for tandem reactions is thoroughly reviewed by **Liu** and collaborators in China, who offer an updated outline on the construction of chiral molecular catalysts used for enantioselective tandem reactions, and a perspective for the further development of silica-supported molecular catalysts for tandem reactions.

A joint Iran–South Korea team led by **Safaei** immobilized a complex of iron(III) amine bis(phenolate) on silica-coated magnetic nanoparticles affording a magnetically recoverable catalyst suitable for the efficient aerobic oxidation of a wide range of alcohols and sulfides with excellent conversion and selectivity under mild conditions to acids (or ketones) and sulfoxides, respectively. Furthermore, the stability of the structure and morphology of their efficient recyclable system was investigated, and all of the data proved that the complex was anchored firmly to the magnetite nanoparticles.

The issue includes three remarkable photocatalysis studies. In a successful collaborative work between Austria and Thailand, which may ultimately allow for the preparation of a low-cost hydrogen peroxide evolving cathode, **Portenkirchner** et al. report a molecular copper-porphyrin photoelectrocatalyst covalently bound to anodic $TiO_2$ nanotube arrays which under visible light irradiation and under cathodic polarization up to $-0.3$ V vs. Normal hydrogen electrode photocatalytically produces $H_2O_2$ in pH neutral electrolyte, at room temperature and without need of sacrificial electron donors.

**Skorb's** team in St. Petersburg and Semenov at Harvard University describe an interesting strategy to drastically decrease the photodegradation activity of titania coated by a layer assembly of polyelectrolytes (polystyrene sulfonate/polyethylenimine) using the titania inner surface to entrap trypsin enzyme aiming for a photocatalytic regulation of autocatalytic wave.

**Jain** and collaborators in India describe an efficient and low cost photocatalytic process for the oxidative self-dimerization of 2-naphthols under remarkably mild conditions using only visible-light irradiation of the reactant mixture in the presence of a composite catalyst consisting of intercalated $MnO_2$ nanoparticles in reduced graphene oxide(rGO/$MnO_2$). The hybrid photocatalyst exhibits significantly higher activity than $MnO_2$ nanoparticles and rGO.

Overall, the issue shows that the boundaries amongst all formal domains of catalysis—homogeneous, heterogeneous, biocatalysis, and photocatalysis—are becoming more vague or have even disappeared. Contemporary scholars in chemical science use nanochemistry methods to build solid catalysts of activity comparable, or even higher, than the homogeneous counterparts. They then investigate the chemical nature, the structure and the activity of the catalytically active species at the material's intrapore surface by a cornucopia of contemporary analytical methods such as field-emission transmission electron microscopy, field-emission scanning electron microscopy, FTIR spectroscopy, thermogravimetric analysis, vibrating sample magnetometry, ambient pressure X-ray photoelectron spectroscopy, XRD, atomic absorption spectroscopy, nitrogen physisorption, magic angle spinning NMR spectroscopies, chemical transient kinetics analysis, sum-frequency generation vibrational spectroscopy, and elemental analysis.

By progressively filling knowledge gaps, the aim is to produce highly stable catalytic materials for all sort of productions, renewing the solid catalysts used in typical petrochemical processes such as polymer synthesis, to heterogenize all homogeneous catalysts used in fine chemical synthesis, as well as to develop the solid catalysts for the second generation biorefinery that will replace the oil refinery.

Hopefully, this issue, for which we warmly thank all the eminent colleagues who contributed and the editors at *ChemCatChem*, will be an inspirational research and educational tool for the years to come.

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