Science@ifpen
Issue 9 - June 2012

"Catalysis" and "separation" are key skills for environmentally-friendly innovation in the refining and chemicals sectors.

The combination of catalytic steps and separation of products leads to the development of innovative, more energy-efficient processes with better yields and limits the production of by-products. This has a major impact if we consider that 80% of the products we use have undergone one or more catalysis and/or separation steps at some point in their manufacture.

Thanks to its expertise in these fields, IFPEN has become an internationally renowned player: it is consistently one of the world's top publishers and patent filers in the areas of catalysis by sulfides or zeolites synthesis, for example. It thereby makes an active contribution to the development of processes in new fields, such as biofuels, bio-sourced chemistry or CO_2 capture.

This influence is illustrated in this issue of Science@ifpen through a selection of news items taken from recent publications that are the fruit of collaboration with academic partners.

We hope that you enjoy this issue.

Denis Guillaume,
Director, Catalysis and Separation Division

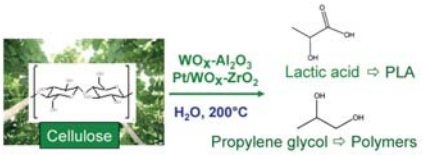
Chemistry goes down to the woods

Recycling renewable raw materials into substances that can be used in fuels and chemicals is a major research priority nowadays. Among the various possible processes, the catalytic transformation of cellulose in aqueous phase is a promising way to obtain valuable products.

However, due to the high crystallinity of cellulose and the fact that it is totally insoluble in conventional solvents, this conversion into high added value products is still a real scientific and technical challenge.

Research under way at IFPEN has demonstrated that, despite these drawbacks, substances of interest in the chemistry sector could be obtained in hydrothermal conditions by partial depolymerization of cellulose[1]. Unfortunately, this reaction is not selective. The use of catalysts with a high Lewis acidity (WO_x-Al_2O_3) not only improves conversion of the cellulose but also makes it possible to guide the reaction towards the production of lactic acid. This effect is thought to be linked to the capacity of Lewis acid sites to coordinate solubilized oligosaccharides[2]. The addition of a metal function (Pt/WO_x-Al_2O_3) on a solid Lewis acid site promotes the formation of propylene glycol, a platform substance for the production of bio-sourced polymers.

The combined action of the hydrothermal medium and specific catalytic sites therefore leads to the production of synthons for the chemistry industry, offering interesting potential for the development of processes to convert lignocellulosic biomass into substances of interest.



Conversion of cellulose into substances of interest.

(1) ***V. Jollet, F. Chambon,*** *F. Rataboul,* ***A. Cabiac,*** *C. Pinel,* ***E. Guillon,*** *N. Essayem, Green. Chem, 2009, 11, 2052. DOI: 10.1039/B915758A*

(2) ***F. Chambon,*** *F. Rataboul, C. Pinel,* ***A. Cabiac, E. Guillon,*** *N. Essayem, Applied. Catal. B, 2011, 105, 171. DOI: 10.1016/j.apcatb.2011.04.009*

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Amines are experiencing high throughput screening

The constant increase in greenhouse gases in the atmosphere has led to the development in recent years of solutions aimed at limiting these emissions and, especially, CO_2.

A significant proportion of CO_2 emissions comes from industrial installations using fossil fuels. The technologies implemented need to be capable of reducing these emissions without penalizing the efficiency of these installations excessively.

Postcombustion CO_2 capture involves a selective extraction from flue gases, but the conditions are not very favorable since the CO_2 is diluted in a non-pressurized atmosphere. The gas sweetening process using amines (for example monoethanolamine or MEA) makes it possible to extract CO_2 through absorption. The resulting solution must then be regenerated at higher temperature, which requires a great deal of energy.

The challenge is therefore to identify molecular structures of amines presenting energy properties that are more efficient than MEA.

In this context, IFPEN has recently developed a high throughput screening (HTS) tool capable of large-scale, rapid evaluation of the thermo-dynamic properties of amines. Its use has led to the properties of almost 150 substances and to identification of structures that are promising in energy requirement for the process.

The tool can also be paired with statistical modeling methods to construct mathematical relationships between the structure of the molecule and the properties of interest. It consequently becomes possible to quickly identify high-potential substances among the various candidates available.

Equipment used for high throughput screening at IFPEN.

F. Porcheron, A. Gibert, P. Mougin, A. Wender, High Throughput Screening of CO_2 solubility in aqueous monoamines solutions, *Environmental Science & Technology, 2011, 45, 2486-2492. DOI: 10.1021/es103453f*

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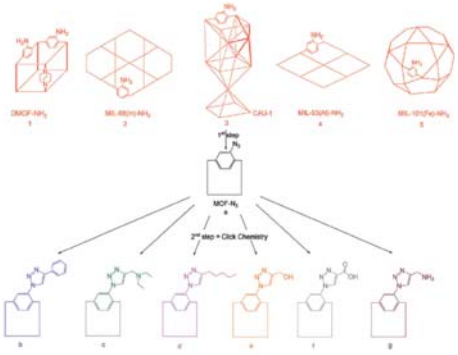
MOFs: a building kit



Strategy to functionalize MOF using a "click chemistry" reaction.

MOFs (Metal Organic Frameworks) are crystallized hybrid materials composed of metal centers linked by organic ligands.

Due to their very high specific surface area and porous volume, this family of materials has attracted the interest of the scientific community in the last decade. Although these properties are of obvious interest for catalysis, most of the research carried out to date has been mainly focused on the synthesis of these materials, their characterization or their applications in fields such as hydrogen storage or CO_2 capture.

To make these materials active, from the catalysis point of view, IFPEN, in collaboration with Ircelyon, has developed an original approach to functionalize their surface using "click chemistry".

This method, which can be applied [1, 2] to MOFs carrying a $-NH_2$ function, consists in coupling an azide function with an alkyne function. Functionalization of several MOFs using a broad variety of organic species becomes therefore possible.

Consequently, the use of "click chemistry" provides access to solids with a wide range of various porosities, carrying specific functions (acid, basic, hydrophobic, etc.), which offer significant potential as catalysts in the fields of fine chemistry or biomass conversion.

*(1) **M. Savonnet, D. Bazer-Bachi, N. Bats, J. Perez-Pellitero, E. Jeanneau, V. Lecocq, C. Pinel, D. Farrusseng,** J. Am. Chem. Soc., 2010, 132 (13), 4518.*

*(2) **M. Savonnet, E. Kockrick, A. Camarata, D. Bazer-Bachi, N. Bats, V. Lecocq, C. Pinel, D. Farrusseng,** New J. Chem., 2011, 35, 1892.*

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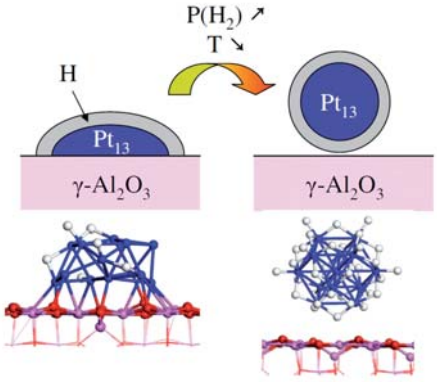
Quantum calculation to break the code of catalysts

Sub-nanometric metal particles (size close to or less than one nanometer) deposited, on an oxide substrate, are used as heterogeneous catalysts for numerous reactions, such as catalytic reforming[1]. Optimizing these on the basis of process (T,P) conditions demands an in-depth knowledge of the environment of the atoms making up the active phase. Their observation is nonetheless made difficult by their very small size. *Ab initio* quantum modeling is therefore an ideal tool to aid resolution of their structure in the reaction medium.

IFPEN, in collaboration with ENS Lyon, performed quantum calculations coupled with a thermodynamic approach to understand the evolution of the structure of platinum particles on a γ-Al_2O_3 substrate[2]. Under low hydrogen pressure, the calculations demonstrate that an aggregate of 13 platinum atoms presents a biplanar morphology with a metallic character, as expected to be found in reforming catalysts. Under high hydrogen pressure, the particle is reconstructed as a cuboctahedron, which increases the hydrogen-particle interaction to the detriment of the metal-substrate interaction. This reconstruction allows the aggregate to stabilize a large number of H ions per Pt. These results are quantitatively related to the results of hydrogen chemisorption experiments.

Quantum calculations applied to heterogeneous catalytic systems therefore make it possible to gain a better understanding of how they evolve in operating conditions in order to propose avenues for improvement, particularly in the case of very small metal particles.

Current research is focusing on modeling the reactivity of aggregates of this type in the presence of hydrocarbon molecules.



Model of the reconstruction of a Pt_{13} aggregate on a γ-alumina substrate in H_2 atmosphere.

(1) ***A. Jahel, P. Avenier, S. Lacombe,*** *J. Olivier-Fourcade, J.C. Jumas, J. Catal., 2010, 272, 275. DOI: 10.1016/j.jcat.2010.04.007*

(2) ***C. Mager-Maury, G. Bonnard, C. Chizallet,*** *P. Sautet,* ***P. Raybaud,*** *ChemCatChem, 2011, 3, 200. DOI: 10.1002/cctc.201000324*

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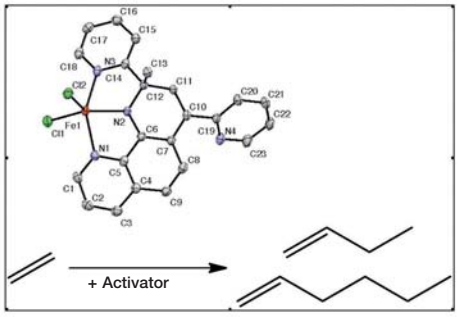
Iron is best

Short-chain alpha-olefins, such as 1-butene (C4), 1-hexene (C6) or 1-octene (C8) are important chemical intermediates. These substances are, among other applications, used as comonomers in the production of polyethylene. They are primarily obtained from ethylene via catalyzed oligomerization reactions.

Existing industrial processes generally lead to broad distributions of olefins (C4-C20+) that do not really suit market demand, rather oriented towards light olefins (C4-C8).

The dual scientific challenge is therefore to control the distribution of the olefins formed, while at the same time using catalysts based on widely available metals with low toxicity. Against this background, IFPEN developed new, homogeneous iron oligomerization catalysts. The first step was the discovery of versatile N,N,N nitrogenous ligands based on the dihydro-phenanthroline skeleton, as well as the development of a simple and selective process for access to these ligands[1]. The first iron(III) complexes associated with these ligands were then isolated and characterized[2]. After activation, these complexes form stable systems that catalyze the oligomerization of ethylene with a high level of selectivity for butenes (98% 1-butene) and hexenes[2].

Research is continuing in order to optimize these catalysts and explore their potential.



N,N,N ligands and corresponding iron(III) complexes. Application to ethylene oligomerization.

(1) ***C. Rangheard, D. Proriol, H. Olivier-Bourbigou,*** *P. Braunstein, Dalton Trans, 2009, 770. DOI: 10.1039/b817726k*

(2) ***A. Boudier, P-A. Breuil, L. Magna, C. Rangheard, J. Ponthus, H. Olivier-Bourbigou,*** *P. Braunstein Organometallics, 2011, 30, 2640. DOI: 10.1021/om200197s*

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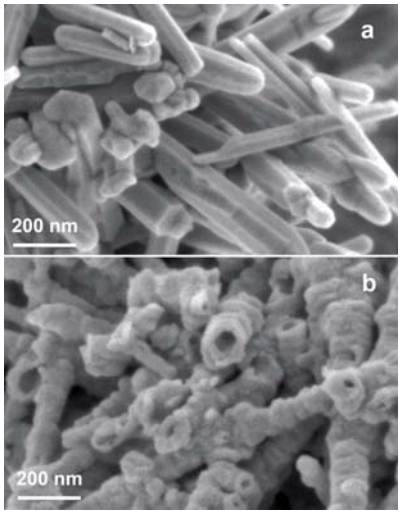
Syngas purified on Zinc

The BtL (Biomass to Liquids) process aims to convert lignocellulosic biomass (wood, agricultural residues, etc.) into second-generation fuels (biodiesel and biokerosene). The process involves an initial gasification step to turn the biomass into a syngas, consisting of a mixture of CO and H_2, followed by a Fischer-Tropsch reaction to produce liquid hydrocarbons. In so far as the catalysts used for this reaction are extremely sensitive to the presence of sulfur, desulfurization of the syngas is a key step.

ZnO is one of the principal oxides that can be used in final gas desulfurization processes. It combines with sulfur in the presence of H_2S, leading to the formation of ZnS, which remains trapped in the desulfurization reactor. At present, numerous industrial gas desulfurization processes exist, but their performance could be improved by gaining a better understanding of the mechanisms involved in the conversion of ZnO into ZnS.

Research works conducted at IFPEN in partnership with the SPIN Centre of the École des Mines in Saint-Etienne have led to characterization of the physico-chemical phenomena involved in the ZnO sulfidation reaction. In particular, an identified mechanism is based on external growth of the ZnS phase on the initial ZnO particles. This mechanism leads, in particular, to the formation of ZnS particles containing cavities, phenomena which limit the reaction kinetics.

Understanding the reactional mechanisms has led to the construction of a kinetic model taking into account the key parameters affecting the ZnO sulfidation rate and hence the performance of an industrial solid. Ultimately, the knowledge acquired made it possible to define rules for the design of materials presenting optimal properties, thereby improving the efficiency of desulfurization processes.



Scanning Electron Microscope images of ZnO particles before (a) and after sulfidation (b).

L. Neveux, D. Chiche, D. Bazer-Bachi, *L. Favergeon, M. Pijolat,* New insight on the ZnO sulfidation reaction: evidences for an outward growth process of the ZnS phase, *Chemical Engineering Journal, 2012, 181-182, 508-515. DOI: 10.1016/j.cej.2011.09.019*

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Participation in six IEEDs

IFPEN is contributing to four of the seven projects selected on 9 March as part of the 2nd IEED (Instituts d'Excellence en matière d'énergies décarbonées - *Excellence Institutes initiatives in the field of low-carbon energies) call for projects. The themes concern: marine energies (France Energies Marines), 3rd-generation biofuels (GreenStars), low-carbon vehicles (VeDeCoM) and geological CO_2 storage (Géodenergies). In 2011, the Pivert and Indeed IEEDs involving IFPEN had already been selected.*

Upcoming scientific events

• *IFP Energies nouvelles' "Rencontres scientifiques" event* ***– Colloids and Complex Fluids –*** *17-19 october 2012, IFPEN Rueil-Malmaison.*

• *IFP Energies nouvelles' "Rencontres scientifiques" event* ***– IFAC Workshop on Engine and Powertrain Control, Simulation and Modeling, E-COSM'12 –*** *23-25 october 2012, IFPEN Rueil-Malmaison.*

Awards

• **Emmanuelle Guillon,** *IFPEN engineer in the Catalysis and Separation Division, has been awarded the SCF DivCat prize for "her remarkable contribution to acid-base catalysis and the quality of her recent research in the field of biofuels" (5 March 2012).*

• **Thomas Dutriez,** *PhD student, has been awarded the IFPEN thesis prize (Yves Chauvin prize) for his thesis on the theme of "Multidimensional chromatography: towards extensive molecular characterization of vacuum distillate-type feedstocks and an understanding of their reactivity to hydrotreatment" (23 November 2011).*

• **Mickaële Le Ravalec-Dupin,** *IFPEN expert in the Reservoir Engineering Division, has been awarded the Grand prix Michel Gouilloud Schlumberger 2011 prize by the French Academy of Sciences in recognition of the original geostatistical methods that she has developed (22 November 2011).*

Appointments

• **Olivier Appert,** *Chairman and CEO of IFPEN, has been elected as a member of the Académie des technologies (10 January 2012).*

• **Sophie Jullian,** *Scientific Director of IFPEN, has been appointed a member of the Ademe Scientific Board (10 January 2012).*

• **François Kalaydjian,** *Assistant Director of the Resources Business Unit, has been appointed to the "Ground and underground risks" committee of Ineris (1 March 2012).*

• **Xavier Montagne,** *Assistant Director of IFPEN's Scientific Management, has been appointed to the "Accidental risks" committee of Ineris (1 March 2012).*

Managing editor: Marco De Michelis
Editor-in-chief: Sophie Jullian
Editorial committee: Xavier Montagne, Emmanuelle Hutin
Graphic design: Esquif
ISSN No. 1957-3537

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