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Issue 47 - March 2022

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News

Fundamental Research

In the context of an energy environment in full transition, the Catalysis, Biocatalysis and Separation division is redoubling its research efforts on innovation. Alongside applications within IFPEN's traditional scope, the Institute's drive for diversification over several years is beginning to bear fruit, with major benefits in new energy technologies (NET), such as catalysts or biocatalysts for the production of bioproducts or biofuels (biobutadiene, biochemical production of ethanol), and separation agents for the extraction of lithium. This ongoing effort is part of IFPEN's new strategic priority "Climate, Environment and Circular Economy".

To capitalise on the results of this research, IFPEN has relied on a strategy of solid industrial property, with 273 patents filed during the 2016-2020 period (42% of them in NET).

With the aim of offering new technological solutions, this innovation strategy is based on fundamental research, which is critical in overcoming a number of knowledge barriers, such as the understanding of new reaction mechanisms, exploration of new catalysts, photocatalysts and separation agents, decoding biocatalysts. Digital technology is also opening up significant avenues for improvement, with the improved visualisation of experimental data and quantum molecular modelling approaches combined with artificial intelligence.

The scientific merit of this research has been supported by the many papers published from 2016 to 2020, in connection with national and international academic partnerships, and with the recognition of 12 prestigious awards in the same period.

The division has also implemented a highly proactive policy of outreach, playing a role in national and international networks, contributing to a range of collaborative projects (national and European), and steering an industrial chair financed jointly with IDEXYLON.

This special edition of Science@ifpen highlights the recent scientific achievements made by the division in a number of priority areas of its fundamental research.

Luc Nougier
Director of Catalysis, Biocatalysis and Separation

Pascal Raybaud
Scientific Assistant to the Director of Catalysis, Biocatalysis and Separation

LES BRÈVES

Most frequently, the use of a microorganism in the production of biofuels or biosourced chemicals requires its optimisation. This is achieved through genetic engineering, which involves inactivation and/or addition of one or more genes, to improve the ability of this microorganism to produce a target molecule. Identifying genetic engineering strategies requires a solid knowledge of the complex biological systems in which the improvement is needed.

The explosion of “omics” analysis techniques over the last twenty years has made it possible to identify and quantify the biological molecules that make up a cell in their totality and to gain a better understanding of their phenotype (the observable behaviours, e.g. the production of a molecule of interest). Now, multiple levels of data can be collected to establish the relationship between the various macromolecules (DNA, RNA, proteins, metabolites) of a biological system (figure).

At IFPEN, access to **genomics** (**DNA**) has helped in gathering data on the composition and structure of the genomes of the microorganisms used in the Biotechnology division [1,2]. This means we can now accurately map the genetic code of the industrial strains produced, then link it to the phenotypes observed.

Click on the picture to enlarge

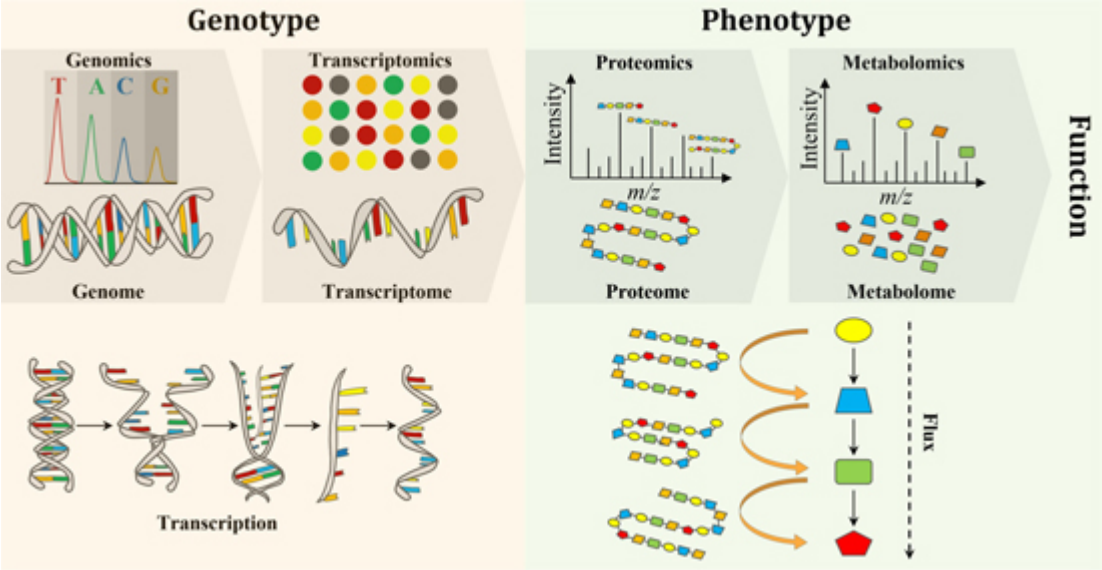

Figure: Overview of the flow of molecular information, from the gene to the function and phenotype, and the “omics” techniques that allow their analysis [3].

The following stages of analysis involve monitoring the expression of the thousands of genes of a micro-organism and the synthesis of their product, through **transcriptomic (RNA), proteomic (proteins) and metabolomic (metabolites)** approaches. The tools developed through these approaches [4,5] are now used as standard, including for research theses, in order to answer questions related to the optimisation of our microorganisms. They help to fine-tune our fermentation processes. The results achieved as part of a thesis by Rémi Hocq, who received three awards for his work in 2020-2021, are primarily based on the use of these tools.

More recently, methods of gathering information on the epigenetic regulation[a] of gene expression were developed as part of another doctoral paper. **Epigenomic** data have made it possible to identify previously unknown regulation mechanisms involved in the production of cellulases in *Trichoderma reesei*, a model microorganism involved in our lignocellulosic biomass hydrolysis procedures [6].

Finally, research into new enzymatic activities or new microorganisms is carried out through the analysis of complex ecosystems. In this context, **metagenomic** and/or **metatranscriptomic** approaches are deployed. These approaches allow us not only to establish the microbiological composition of a specific biotope - such as an environment that is likely to contain microorganisms of interest, or subsurfaces linked to renewable energy projects (geothermal or hydrogen storage) - but also to identify the enzymes present and the active synthesis routes.

In summary, the use and mastery of “omics” tools at IFPEN has a two-fold effect, giving us a more in-depth understanding of the microorganisms of interest and optimising them for use in breakthrough bioprocesses.

a- An area of biology that studies the nature of mechanisms that modify gene expression reversibly, transferrably and adaptively without altering the nucleotide sequence.

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Glossary

DNA: nucleic acid, carrier of genetic information

RNA: nucleic acid allowing the synthesis of proteins

Metabolite: intermediate organic substance or product of metabolism

Epigenetics: study of the nature of mechanisms that modify the expression of genes without altering their sequence

Metagenomics: the entire set of genes contained in a given biotope, all species combined

Metatranscriptome: the entire set of genes expressed in a given biotope, all species combined

Cellulase: biocatalyst capable of breaking down cellulose (biopolymer)

Scientific contacts: Frédérique Bidard-Michelot, Francois Wasels

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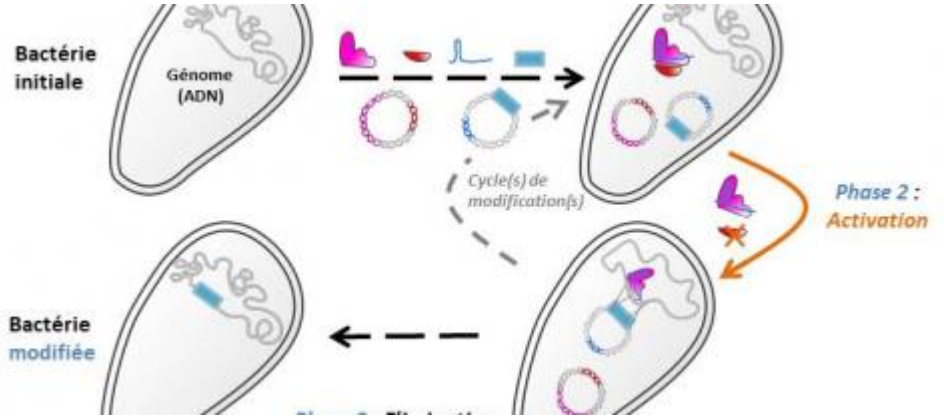
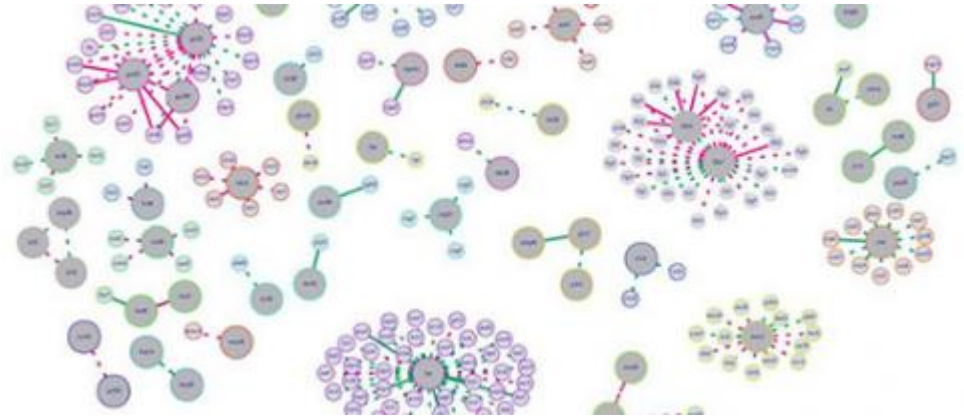


Hydrolysis of lignocellulosic biomass: study of enzyme-substrate interactions (HDR 2015)

The scope of my HDR covered ten years of research at IFPEN within the context of the **development of Futurol™**, a process aimed at producing 2nd-generation bioethanol from lignocellu

Biosciences and biotechnologies | **Microbiology** | **Genomics** | **Biocatalysis**

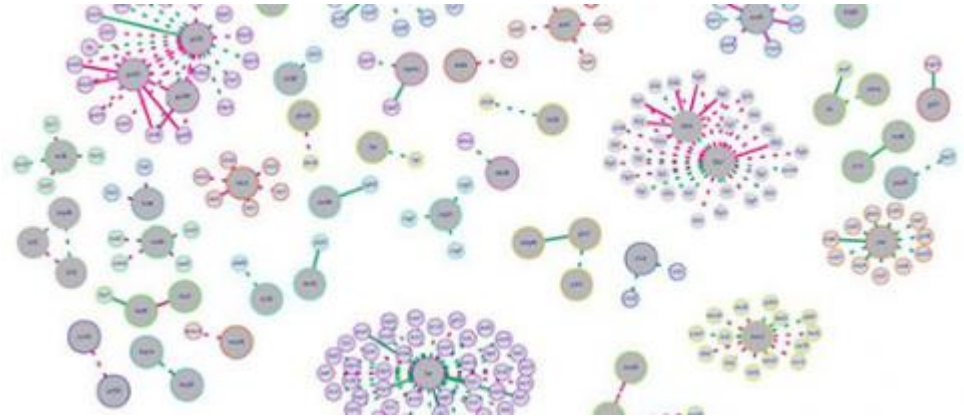


‘‘BRANE Power’’: of genes and algorithms, an alliance for green chemistry

THESIS BY AURÉLIE PIRAYRE, 2018 YVES CHAUVIN PRIZE

Renewable energies | Biofuels and e-fuels

Biosciences and biotechnologies | Genomics | Mathematics and IT | Signal processing/Data science | Bioinformatics



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The “Omics”, seven hired hands working for biotechnology

Chemical theory at quantum level (density functional theory or DFT) is an essential tool in rationalising the reaction mechanisms involved in the preparation of catalysts, as well as in their use, thanks to the optimisation of their activity [1,2]. IFPEN has carried out a number of projects aiming to shed light on these catalysts, which are of particular interest to industrial processes [3,4,5], but until now, very little work has been done on simulating the key preparation steps of the heterogeneous catalysts.

The fundamental research work of the "*Rational Design for Catalysis*" (ROAD4CAT) chair, carried out in partnership with ENS-Lyon and Claude Bernard Lyon 1 University aims to overcome this challenge. Through a combined approach of identification by NMR and DFT simulation, their work has furthered the description of the sites located on the alumina surface [6,7] and identified the patterns of interaction between inorganic phosphorus additives and the surface [8]. These results provide key insights in order to optimise the deposit of active phases on a surface such as alumina. Additionally, where the activation of catalysts is concerned, the simulation of the mechanisms involved in transforming molybdenum oxide olygomers into tri- and di-sulphides (MoS_3 and MoS_2) has made it possible to identify the rate-limiting steps, as well as the margins for improvement [9].

A second challenge tackled by the ROAD4CAT chair is the use of advanced quantum approaches to predict the opto-electronic properties of materials for the photoreduction of CO_2. The identification of MoO_3-$_x$$S_x$/$MoS_2$ or TiO_2/MoS_2 bidimensional heterojunctions has provided clues to identifying innovative materials that can be used to direct charge separation (electron holes) by "Z-scheme" processes inspired by photosynthesis [10].

As part of another research project (Eyring Project), it has been possible to predict the activity and selectivity in hydroconversion of n-heptane, catalysed by a large-pore zeolite, thanks to the combination of high-throughput experimentation (HTE) and microkinetic *ab initio* modelling [11]. Beyond refining, such an approach could also have applications in plastics recycling processes through the deployment of similar mechanisms.

A third research project is currently under way to tackle the methodological challenge of improving the calculation of the kinetic constants of reactions. Carried out in partnership with the Comenius University of Bratislava, the University of Nancy Lorraine, The Ecole des Ponts ParisTech and INRIA, its approach combined quantum molecular dynamics with AI algorithms, in order to increase both the speed and accuracy of calculation of these constants.

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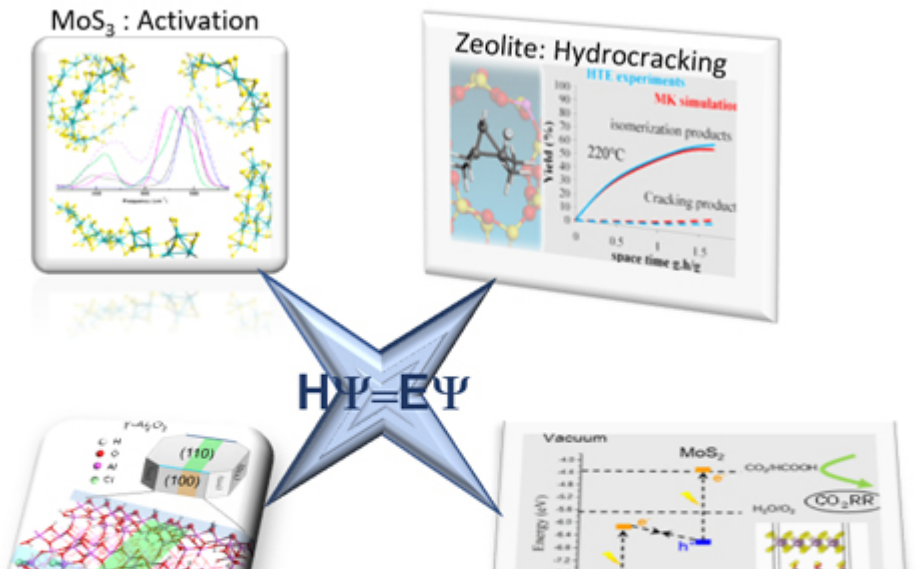

Scientific Production

In the period from 2016 to 2021, IFPEN's Catalysis, Biocatalysis and Separation division published some 50 papers in relation to these molecular modelling approaches. In addition, doctoral works carried out by Kim Larmier and by Jérôme Rey were awarded the Yves Chauvin Prize in 2016 and 2020 respectively.

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News March 2021

Molecular simulation methods contribute to the understanding of the early stages of zeolite synthesis

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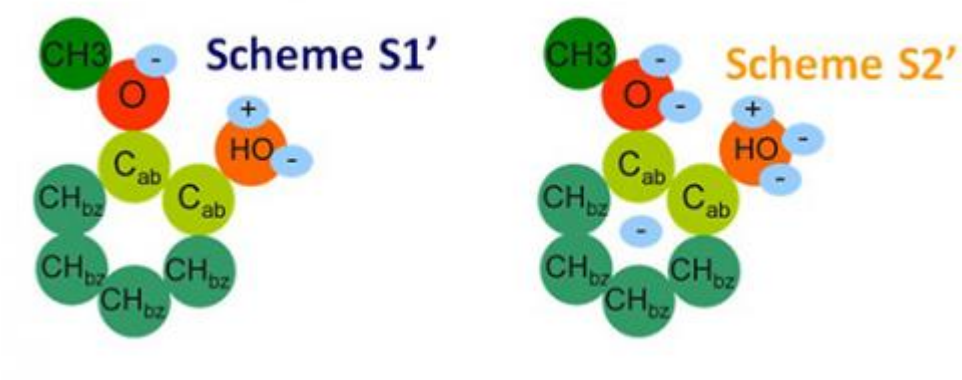
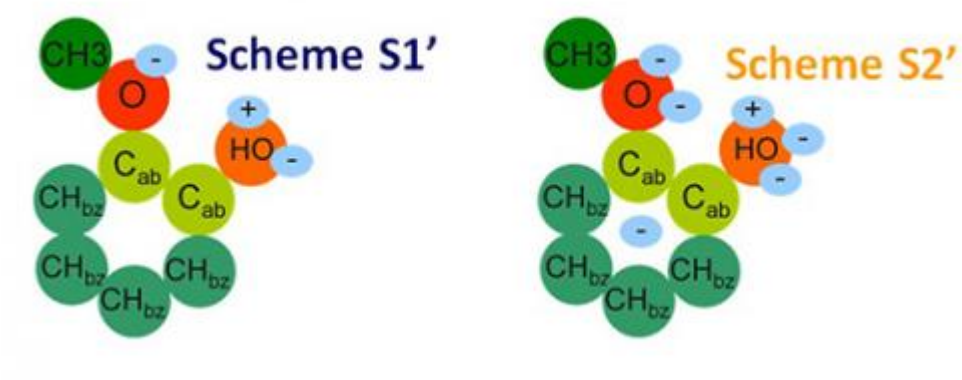
Thermodynamics/Molecular modeling



Review of a Chair on “thermodynamics for biomass fuels”

Unlike hydrocarbons of fossil origin, the molecules derived from biomass are polar, due to the heteroatoms they contain. This difference on a molecular scale induces a more complex macroscopic behavior that must be taken into account when designing the processes where such mixtures are encountered.

Physical Sciences | **Thermodynamics/Molecular modeling**



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Physical Sciences | **Thermodynamics/Molecular modeling**

Molecular modelling: a key tool for current and future heterogeneous catalysis

With emissions from human activity crossing the threshold of 40 billion tons of CO_2 per year, and despite half of the gas being captured by the oceans and land vegetation, in April 2021 its atmospheric concentration reached the unprecedented level of 420 ppm. Although the climate crisis makes the reduction of CO_2 emissions a matter of urgency, some industries will have difficulty in avoiding them, such as cement plants (where the core process is currently based on the calcination of $CaCO_3$) or refineries, which are currently highly energy-intensive. Hence the huge potential interest in procedures that could capture the CO_2 released directly from the plant, where it is most concentrated (at several dozen percent), then recover it at a fraction of the energy cost.

One of the most effective ways of doing this is inspired by photosynthesis and involves converting the CO_2 into valuable molecules with the help of the sun's plentiful and renewable photon energy.

With this in mind, IFPEN is working on the development of a technology that could be fitted to plant exhaust chimneys, or directly to the process exhaust, which uses photocatalysis to treat an effluent that is rich in CO_2 (combustion, reaction gases, etc.) but also in H_2O. The target process is based on the use of solid photocatalysts that operate in gas phase, thereby removing the need for any solvent or sacrificial molecule[a]. As an example, it would allow the photoreduction of CO_2 into chemical intermediates, such as carbon monoxide (CO), methane (CH_4) or even ethane (C_2H_6).

The division's historic effort in this area was recently recognized with the award of the 2021 IMT-Académie des Sciences Young Scientist Prize to Antoine Fécant, a pioneer in the subject at IFPEN.

Currently, four key areas are being worked on simultaneously:

- The development of new solids [1,2] which, thanks to their semi-conductive and catalytic properties, will make it possible to achieve the desired conversion. These efforts are being carried out as part of thesis projects in collaboration with ITQ Valence[b] on the development of new sulphur-containing zeolites, and with ETH Zurich[c] on the development of new transition metal oxysulphides.

- The modelling and prediction of the opto-electronic properties of different solids [3] to assist in the selection of the most promising materials, as part of the ROAD4CAT chair, in partnership with ENS Lyon.

- The development of *in operando* analyses in collaboration with LCS Caen[d], in order to identify charge carriers[e] and reaction intermediates, with the aim of identifying the reaction mechanisms of the photoreduction of CO_2.

- The design of an effective photoreactor that would make it possible to minimize the footprint of the process.

Click on the picture to enlarge

Figure: Pilot laboratory for photoconversion of CO2

In addition to doctoral theses, IFPEN is involved in this topic through joint projects, such as:

- at national level in France, in the ANR PMCOCAT project, coordinated by the Institut Lavoisier de Versailles, which was launched in 2022, and for which IFPEN will conduct testing on new composite materials with strong potential for CO_2 reduction;
- at European level (Horizon 2020 programme), in the SUN2CHEM project, which started in 2020 and brings together 15 partners around the Ecole Polytechnique Fédérale de Lausanne, for which IFPEN will perform life cycle analyses (LCA) of processes aimed at the photo(electro)reduction of CO_2.

After more than a decade of research on photocatalysis, IFPEN has filed some thirty patents in this area, in particular relating to promising materials such as 3D photonic sponges, which should provide a solution to the challenge of reducing the footprint of CO_2 photoconversion processes.

Furthermore, in 2021, IFPEN developed a new research facility for photo-conversion (figure), the only one of its kind in France, thanks to a broad range of parameters that make it possible to adjust variables, such as temperature, pressure, gas flows, irradiation wavelength, radiation output, etc. This tool can be made available to any laboratory wanting to test new materials of interest for the target application.

a- Proton Donor
b- Thesis by Beatriz Silva-Gaspar (2019-2022)
c- Thesis by Sébastien Roth (2021-2024)
d- Thesis by Joudy Dankar (2020-2023)
e- Electrons or holes

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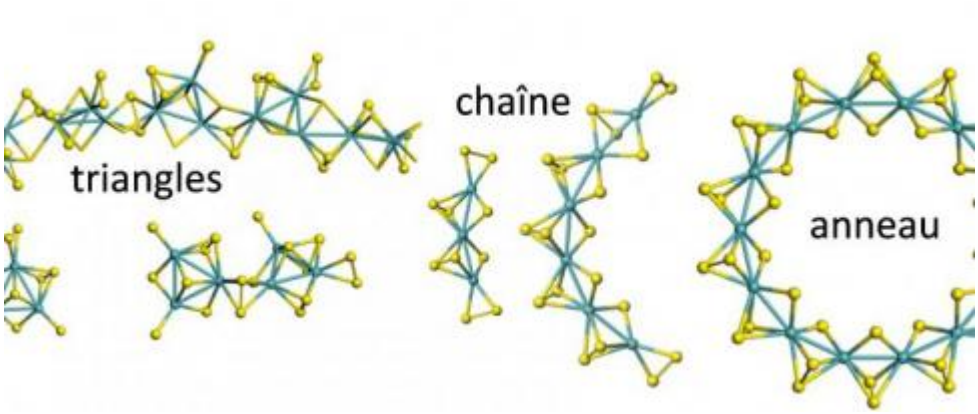

The ROAD4CAT chair one year in

The 1st industrial chair within the IdexLyon project[a], **ROAD4CAT** (RatiOnAl Design for CATalysis), launched in June 2018, brings together IFPEN and the Chemistr

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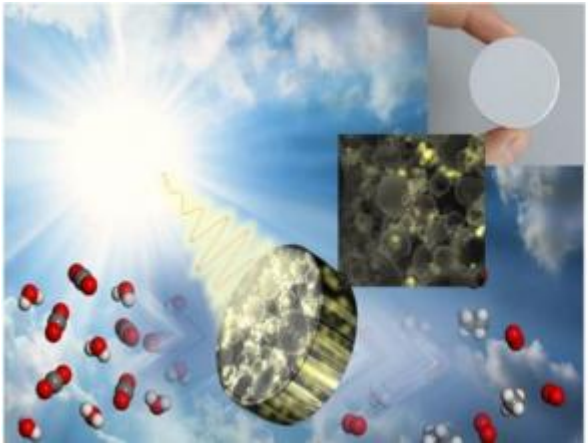


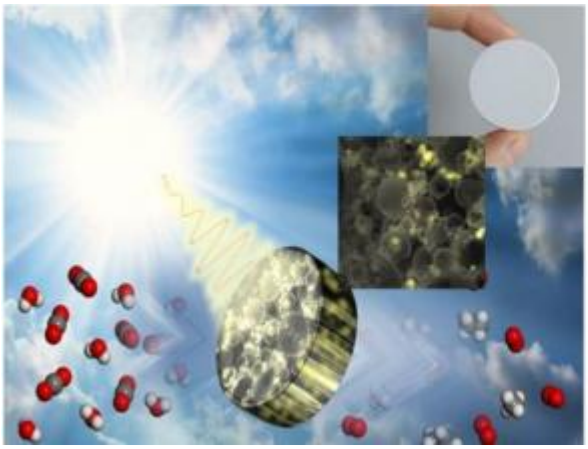
Fundamental Research

News January 2019

Solar fuels: 3D photonic sponges for enhanced CO2 valorization

Press release

Renewable energies



Fundamental Research

News January 2019

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Press release

Renewable energies

Chemical sciences

Photocatalysis, a lighted pathway for CO2 conversion

Driven by the global challenge of switching to a more sustainable economic and energy model, IFPEN has been studying for a number of years biosourced products with high added value and working to develop processes for biomass recovery, as an alternative to conventional petrochemistry.

Sugars are one of the main components of lignocellulosic biomass, a key resource due to its non-competition with food production. In processes, they can react in different ways in order to obtain either motor fuels, or high added-value products such as furfural, ethylene glycol, propylene glycol or glycerol. Consequently, a major challenge in the conversion of these sugars lies in achieving optimal selectivity towards the desired products, hence the need of understanding the reaction mechanisms and the active species. In particular, the key factors at the molecular level that explain the selectivity of a specific catalyst towards a given reaction remain poorly understood.

As a monomer of cellulose and hemicellulose, glucose is the most abundant sugar of lignocellulosic biomass. It is the precursor of many different molecules with strong potential, through various catalytic conversions (figure 1). A doctoral thesis currently under way at IFPEN aims at gaining an understanding of and explain this particular selectivity of tungsten-based (W) catalysts in the conversion of glucose [1]. In fact, these catalysts effectively promote the reaction of retro-aldolisation, a key step in the production of ethylene glycol or short-chain synthons from sugars.

Through a combination of experimental techniques[a] and molecular modelling by DFT[b], we have been able to demonstrate the formation of specific complexes between sugars and metallic species, while also establishing the links with the various possible reaction pathways. In particular, the presence of multiple dinuclear complexes of tungsten has been shown (figure 2) and seems to be responsible for an epimerisation reaction, different to the retro-aldolisation reaction expected. In addition to this, it was also possible to propose transient mononuclear species for this retro-aldolisation reaction. X-ray absorption spectroscopy studies, as well as catalytic tests performed in various atmospheres, have also made it possible to specify that an oxydation degree of +VI is needed in tungsten species in order to effectively catalyze the reaction.

These mechanistic studies have motivated another project, which aims at studying the selectivity of the same reactions in the conversion of sugars, catalysed by zeolites displaying Lewis acidic sites[c]. This project will be carried out from 2022 to 2025 as part of ANR's JCJC programme[d], and will also combine theory and experimentation work.

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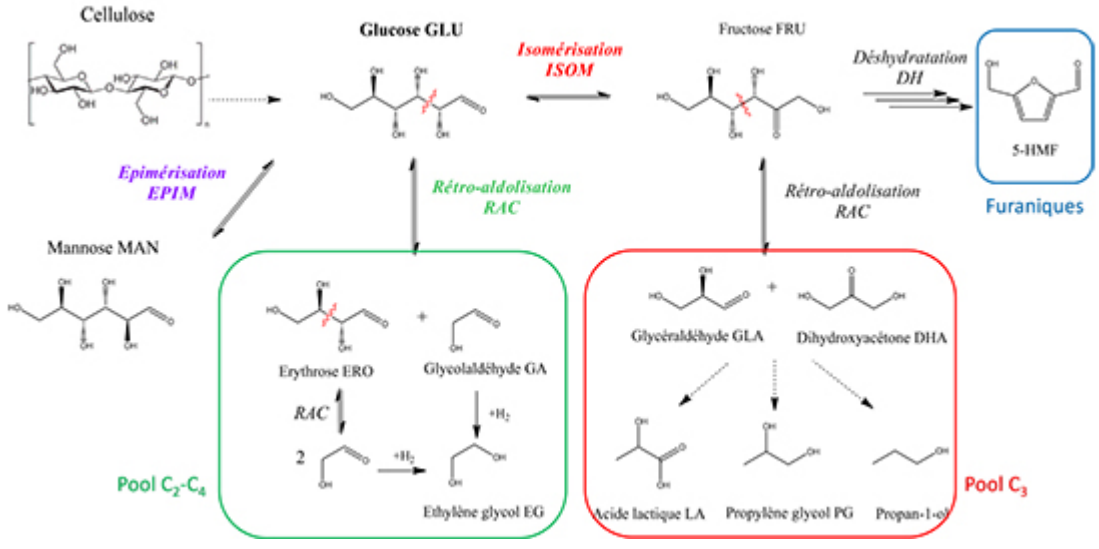

Figure 1: Simplified reaction scheme of the conversion of glucose.

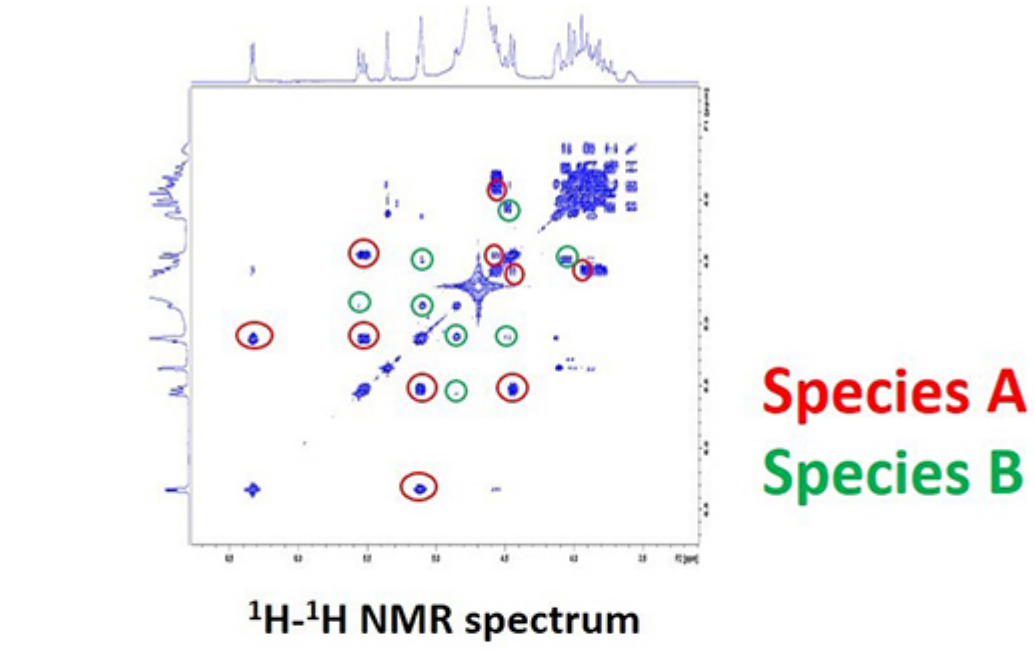

Figure 2: Complexes formed between mannose and the metallic precursors of Mo and W.

a- Including NMR spectroscopy in liquid state, kinetic measurements of the catalytic conversion of glucose and the *in situ* X-ray absorption spectroscopy
b- Density Functional Theory
c- Electron-accepting sites, allowing the formation of a covalent bond with electron donnor species (Lewis bases)
d- Young researchers

Reference:

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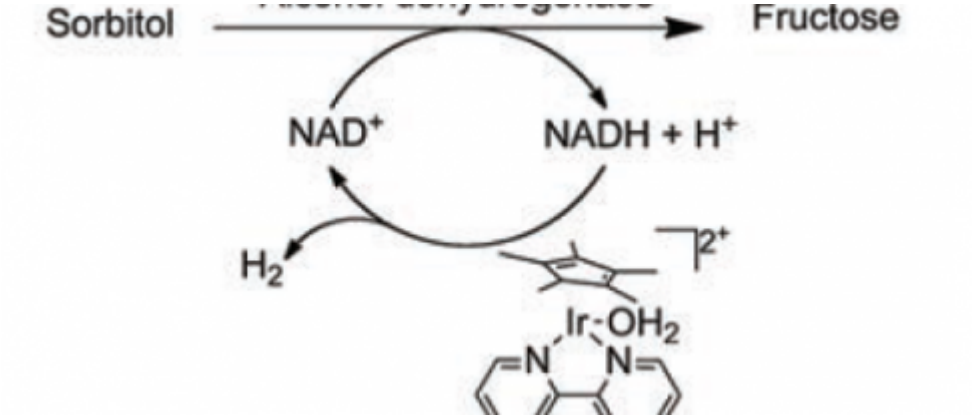

Hybrid catalysis can better deal with bio-based substances

THÈSE DE MARIE GUEHL

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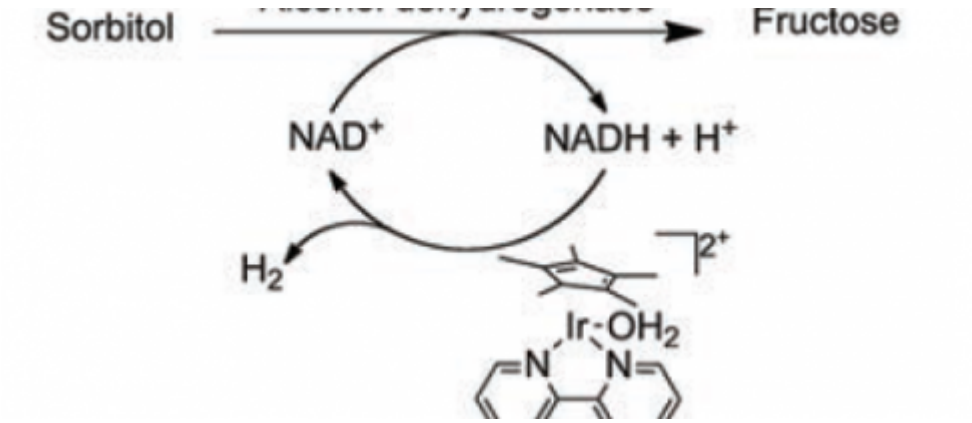

Hybrid catalysis can better deal with bio-based substances

THÈSE DE MARIE GUEHL

Sustainable mobility | Renewable energies | Biofuels and e-fuels | Bio-based chemistry

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Experimentation and modelling combined to study the catalytic conversion of biomass-derived sugars

Zeolites are microporous crystalline aluminosilicates that exist in the natural state and can also be synthesised for a wide range of applications, from the biomedical industry to the production of renewable energy. The introduction of germanium during the synthesis process has made it possible to obtain new zeolite-type solids, which have the advantage of pores that are often larger, giving them significant potential for use in catalysis. In fact, these large pores are accessible by molecules of a larger size, which opens up prospects for conversion of bulky molecules, such as those present in some petroleum fractions or in biomass.

However, these silicogermanates exhibit very low amounts of acid sites, while many reactions are catalysed by acid sites, and they are often unstable in aqueous state, which poses a barrier to their use. Post-treatment stages are therefore needed to acidify the silicogermanates and stabilise them.

A study by numerical simulation, using density functional theory (DFT), has initially demonstrated the thermodynamic feasibility of the stabilisation process [1]. This was then confirmed by experiment, thanks to the silicon enrichment of the zeolite framework, achieved by treatment in gas phase (with $SiCl_4$) [2,3], before incorporation of aluminium in aqueous phase (with a compound known as PAC), which is designed to acidify the solid (figure a).

This work was carried out entirely at IFPEN as part of a doctoral thesis* and has resulted in a new stable zeolite, named IZM-7 [2,4], produced from silicogermanate IM-12. This solid contains virtually no remaining germanium, but retains its large pore size. The evaluation of its properties for catalysis was carried out in collaboration with Katholieke Universiteit Leuven. The results obtained demonstrate promising behaviour (figure b), in that the catalytic activity in the chosen model reaction is greater than that of conventional zeolites (USY). This work opens up potential avenues for the catalytic use of stable silicogermanate derivatives.

For her work on the paper, doctoral researcher Elsy El Hayek was awarded the 2022 Denise Barthomeuf Prize by the French Zeolites Group (GFZ).

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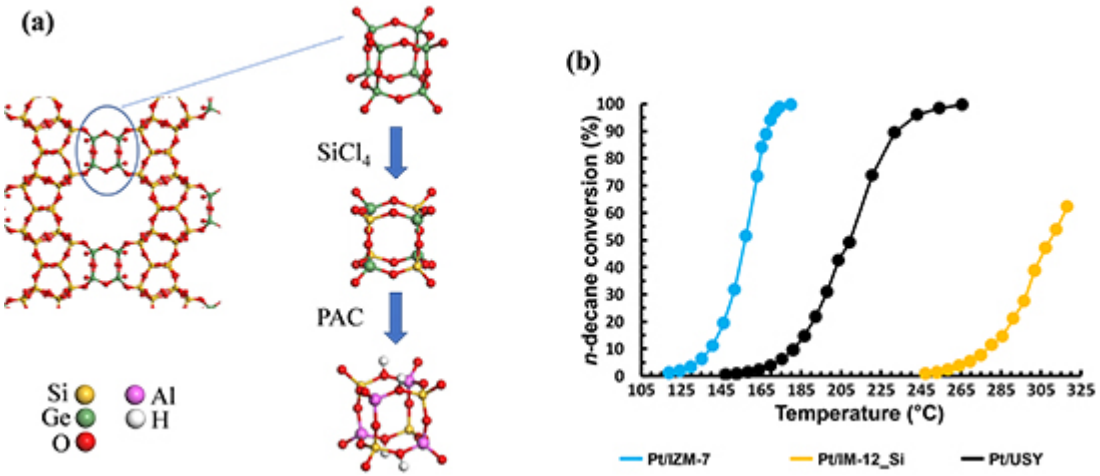

Figure (a): Structure of silicogermanate IM-12 and expected effect of the substitution strategy

implemented.

Figure (b): Catalytic performances in hydroconversion of n-decane on bifunctional catalysts involving a conventional zeolite (USY), the IM-12 zeolite treated with $SiCl_4$ (IM-12_Si) and the new aluminosilicate IZM-7 (the solid is all the more active given the low temperature required to achieve a given conversion).

* Thesis title: “New acid zeolites obtained from silicogermanates”, E. El Hayek, Claude Bernard Lyon 1 University, 2020

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1. ***Ab initio investigation of the relative stability of silicogermanates and their (Alumino) Silicates counterparts***, E. El Hayek, B. Harbuzaru, J. Martens, C. Chizallet, *Microporous Mesoporous Mater. 306 (2020) 110425–110434.*
   >> DOI : 10.1016/j.micromeso.2020.110425

2. ***IZM-7: A new stable aluminosilicogermanate with a promising catalytic activity***, E. El Hayek, G. Vanbutsele, S. Radhakrishnan, M. Rivallan, E. Soyer, C. Bouchy, E. Breynaert, J. Martens, C. Chizallet, B. Harbuzaru, *J. Catal.*
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3. ***Method for stabilisation of microporous silicogermanate in the presence of $SiCl_4$***, E. El Hayek, B. Harbuzaru, C. Chizallet, J. A. Martens, *INPI Number : 3101788, publication date: 16 April 2021.*

4. ***UTL framework-type material with good structural resistance in the presence of water, a high microporous volume and active sites in its framework***, E. El Hayek, B. Harbuzaru, C. Chizallet, J. A. Martens, *INPI Number : 3106130, publication date: 16 July 2021.*

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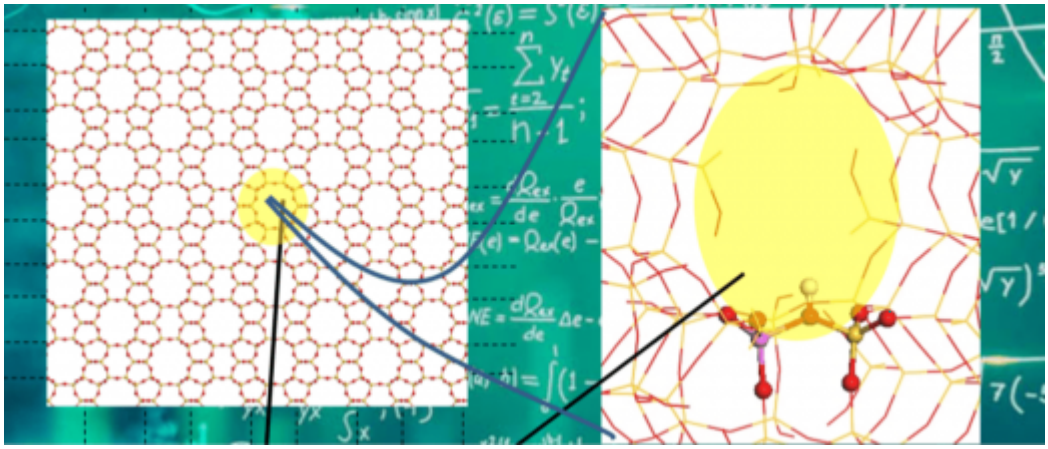

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News November 2020

Shedding light on the external surface of zeolites by quantum calculation

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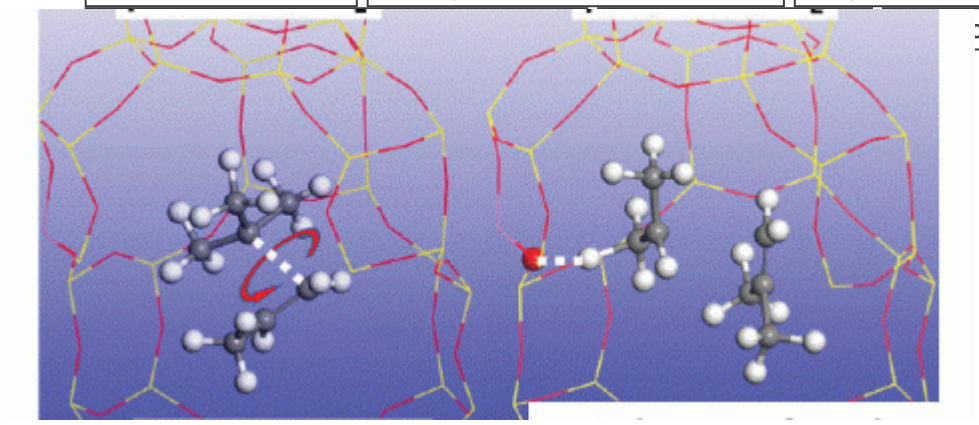

Reaction dynamics in zeolites under the quantum calculation spotlight

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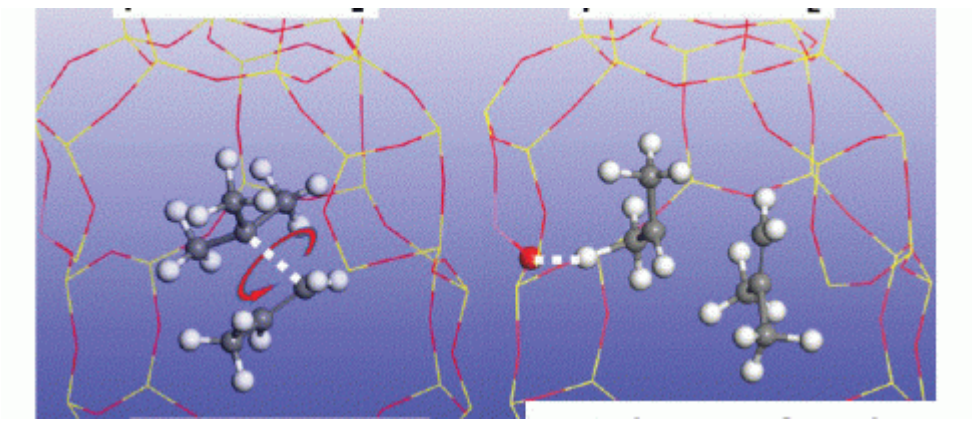

Reaction dynamics in zeolites under the quantum calculation spotlight

Zeolites are nanoporous solids widely used as acid catalysts for the conversion of hydrocarbon molecules. However, determining the rates of the elementary steps of reaction mechanisms...

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New acid zeolites obtained from silicogermanates

The production of biofuels, renewable diesel or sustainable aviation fuel can be achieved through lipid feedstocks conversion, such as vegetable oils, used cooking oils or animal fats. Through a hydrotreatment stage, we obtain long-chain normal paraffins[a], which must then be isomerised or cracked in order to adjust the properties of the effluent, resulting in the specifications required according to the targeted fuel type (particularly cold flow properties and/or final distillation temperature).

These two reactions are carried out on heterogenous catalysts, which are referred to as “bifunctional” as they incorporate a hydrogenating/dehydrogenating function (noble metal or sulphide of a transition metal) and a Brønsted[b] acid function (zeolitic and/or amorphous aluminosilicate). The control of their selectivity is therefore essential in order to direct the reaction towards hydro-isomerisation or hydrocracking.

In bifunctional catalysis, selectivity is heavily dependent on the intrinsic properties of the acid phase, i.e. its porosity and Brønsted acidity, but the hydrogenation/dehydrogenation function is also an important factor. Additionally, the catalyst can only achieve its maximum isomerisation selectivity (for given operating conditions) if the hydrogenating/dehydrogenating function is very strong, i.e. of a noble metal-type. This is what we refer to as a well-”balanced” bifunctional catalyst. However, industrial catalysts are often based on transition-metal sulphides, which are more resistant to the impurities present in the feedstock, but less selective. It is therefore essential to be able to counterbalance the impact of this weak hydrogenation function on the activity and selectivity of a bifunctional catalyst, by optimising its formulation or the operating conditions (pressure and temperature).

As part of a collaboration with IST Lisbon[c], supplemented by work carried out at IFPEN, a study combining experimentation and modelling examined the interdependence between the hydrogenation function and the zeolitic acid function, in the hydroconversion of n-hexadecane [1]. To this end, catalysts were prepared by the impregnation of zeolites with a strongly hydrogenating element: platinum (Pt). These catalysts were then compared with their low-hydrogenating equivalents, based on molybdenum di-sulphide (MoS_2) promoted by nickel.

This work resulted in a kinetic model that is capable of predicting the activity and selectivity of the bifunctional catalyst according to the ratio between metallic sites and Brønsted sites (figure 1). This model is also able to predict the behaviour of a bifunctional catalyst involving two different acid phases, which is a highly attractive feature as it offers the ability to fine-tune the selectivity [2] and determine the effects of operating conditions.

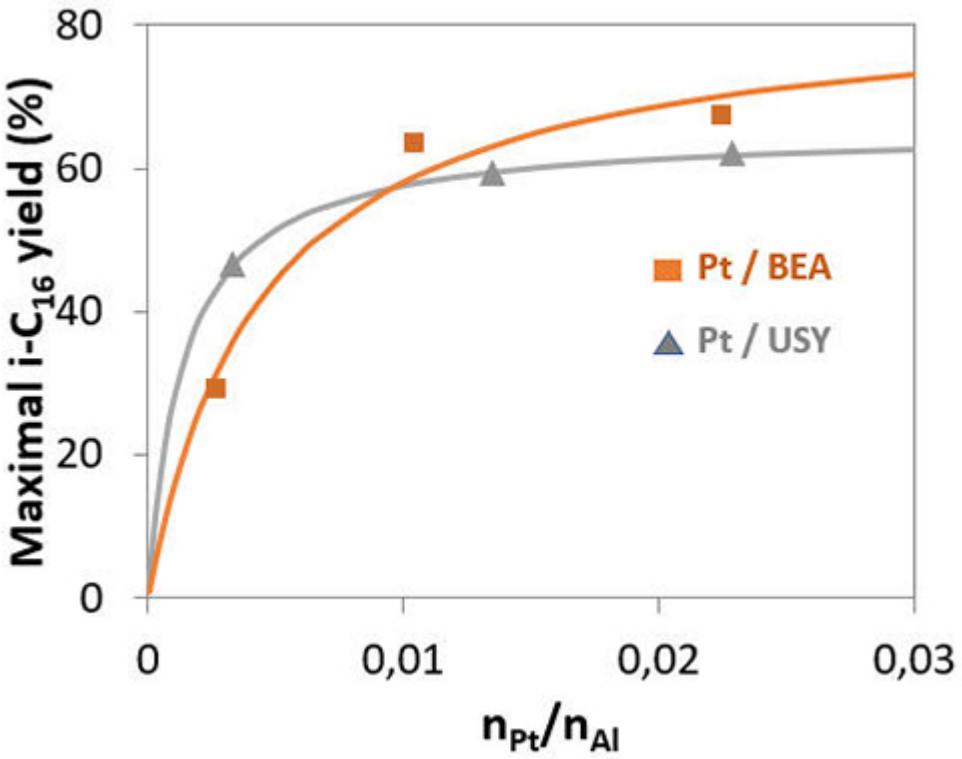

Figure 1: Change in the maximum isomerisation yield (a descriptor of the selectivity in isomerisation, during the hydroconversion of n-hexadecane, according to the ratio between metallic sites (Pt) and Brønsted sites (Al) for two zeolites (HBEA and HUSY) [1].

The comparison of Pt catalysts with nickel-promoted MoS_2 catalysts [3,4], which are poorly balanced and therefore offer low selectivity towards isomerisation, led to the identification of the yield spread with regard to this reaction and further studies on how it can be remedied. Two combined actions could make it possible to achieve a better balance at process level: the addition of ammonia as an inhibitor of acid sites in the feedstock and the reduction of zeolites in the catalyst support (figure 2). To achieve an identical yield to that of a Platinum-based catalyst, the addition of ammonia to the feedstock reduced the concentration of acid sites by around three orders of magnitude. So, in this example, this is the level that must be achieved in order to balance a nickel-promoted MoS_2 catalyst.

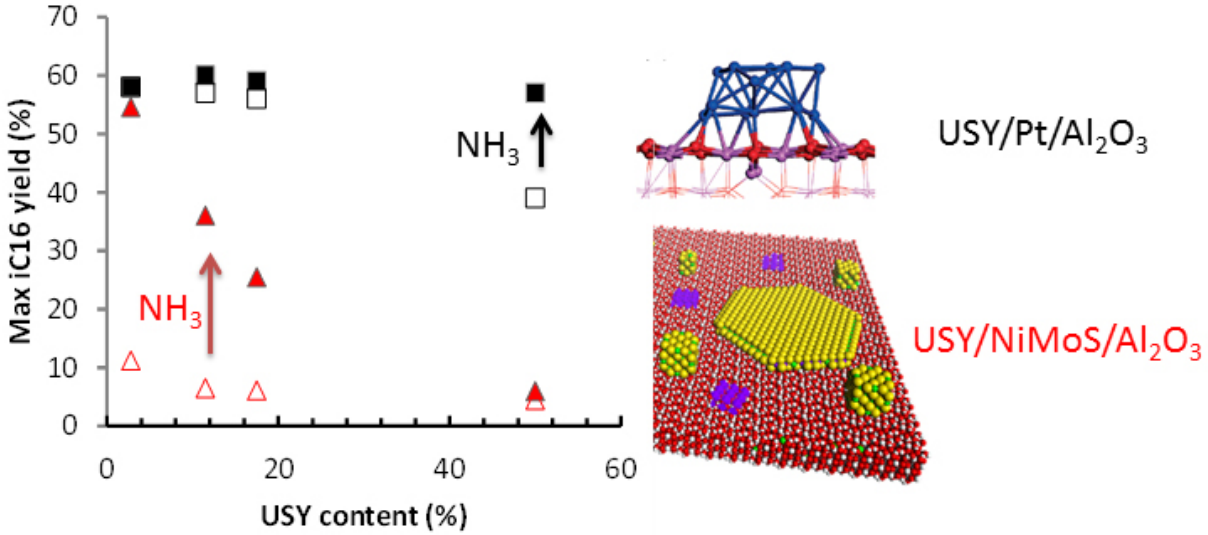

Figure 2: Comparison of Pt-based (black) with Ni/MoS2 catalysts (red). The concentration of acid sites has been modified by varying the USY zeolite content in the extruded product. The figure shows the maximum yield in iC16, in the presence (filled symbols) or absence (empty symbols) of an ammonia inhibitor.

This work has made it possible to quantify the impact of the balance between the hydrogenation function and the acid function of a bifunctional catalyst for the production of biofuels, according to the composition of the catalyst and the operating conditions. Some points that remain partially unclear are still undergoing studies, in particular in relation to the impact of the inhibitors, and the relation between the intrinsic selectivity of the zeolite and the nature of its acid sites.

a- Long-chain linear paraffins (typically more than 10 carbon atoms)
b- “Proton-donor”-type acid
c- Thesis by Pedro Mendes, “Hydroconversion catalysts based on zeolite mixtures, from ideality to reality”, 2017.

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>> DOI: 10.1021/acs.iecr.0c01680

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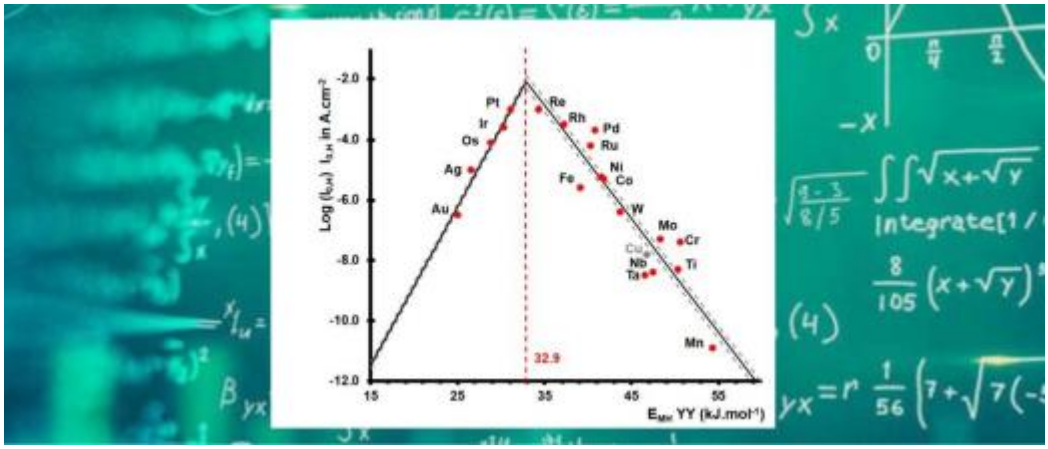

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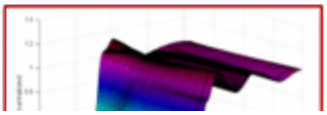

In situ characterization of the genesis of the active sites of hydrotreatment catalysts by X-ray Absorption Spectroscopy

Meeting environmental standards governing the sulfur content of oil-based fuels hinges around the optimization of hydrotreatment processes (HDT), involving, in parti

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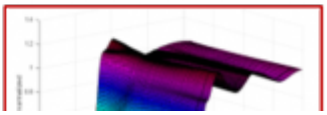

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Bifunctional catalysis deployed for the production of biofuels

Faced with the current climate challenges, alternative fuels are attracting a growing interest for the mobility of the future. Of the various possible alternatives, hydrocarbons could be synthesised via a well-known process: the Fischer-Tropsch (FT) process, based on Syngas (CO and H_2) produced, in particular, by biomass gasification. The FT reaction is a polymerisation of CO and H_2 that involves chain initiation, propagation and termination reactions leading to a distribution of long-chain hydrocarbon products that can contain up to 100 carbon atoms.

However, the deactivation of FT catalysts is a major issue that directly impacts the costs of the process. This loss of activity is accompanied by a drop in selectivity in synthesised long-chain hydrocarbons, which diminishes the fraction of products that can be recovered. The mechanisms responsible for the deactivation are now well documented, while those behind deselectivation are still poorly understood.

To identify these mechanisms, a multiple-stage methodology was implemented as part of a doctoral thesis[a]. Firstly, protocols for accelerated ageing were developed to individually simulate each of the key deactivation phenomena. Then, high-throughput experiments (HTE) implementing these protocols made it possible to characterise their effect on the selectivity of the catalysts. Finally, modelling of the experimental data obtained was used to interpret the phenomena involved at molecular level, via a micro-kinetic model detailing each elementary step of the reaction.

The results show that, among the ageing phenomena observed, the deposition of carbon [1], carburation [2] (figure) and oxydation of the active phase all cause a loss of selectivity in long-chain hydrocarbons, with carbon deposition found to have the most adverse affect. However, carburation stands out from the other phenomena as it causes a simultaneous reduction in selectivity toward olefins.

According to the modelling results, it is the modification of chain propagation and termination reaction rates, due to a change in electronic or steric environment of the active sites, that causes the phenomenon of deselectivation. Finally, a model was proposed that was capable of taking the various mechanisms of deactivation and deselectivation into account, which was then used to process industrial data on Fischer-Tropsch synthesis. The resulting simulations reveal that carbon deposition and carburation provide a quantitative explanation for the loss of selectivity observed in experiments.

The identification, characterisation and modelling of deselectivation phenomena are tools that now make it possible to guide the choice of formulation of catalysts and/or operating conditions of the reaction in order to improve the performance of the Fischer-Tropsch process.

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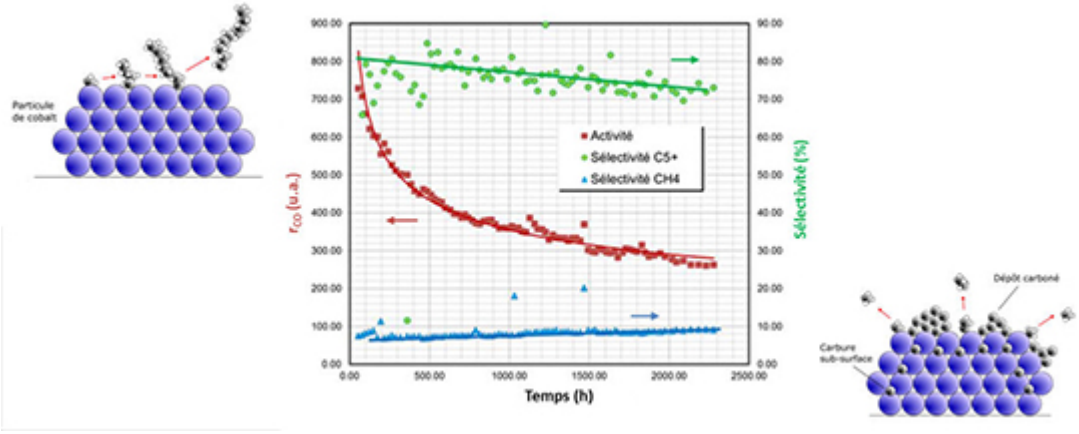

Figure: Deselectivation mechanisms identified in industrial conditions.
Left: chain growth on new catalyst (t=0)
Right: subsurface carburation and coke deposition perturbating chain growth (end of test)

a- Thesis: “Deselectivation in Fischer-Tropsch catalysis: towards an identification of the mechanisms”, P. Hazemann, Claude Bernard Lyon University 1, 2020.

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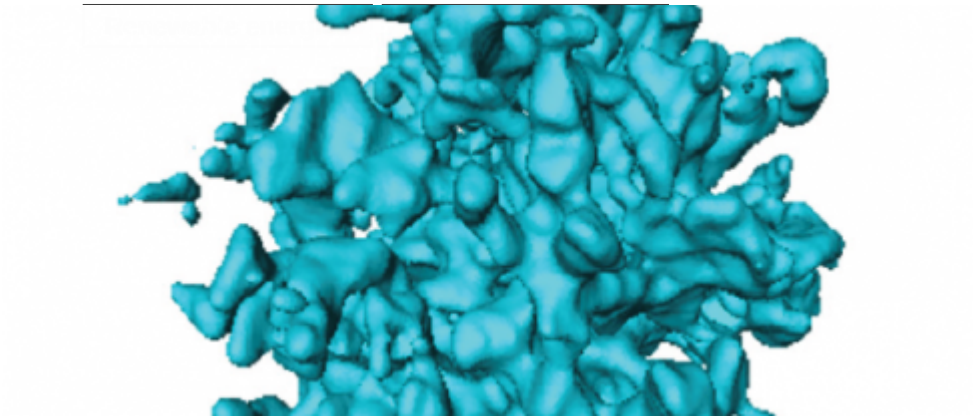

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Fischer-Tropsch synthesis is a catalytic process to produce hydrocarbons from a syngas, which could come from biomass.

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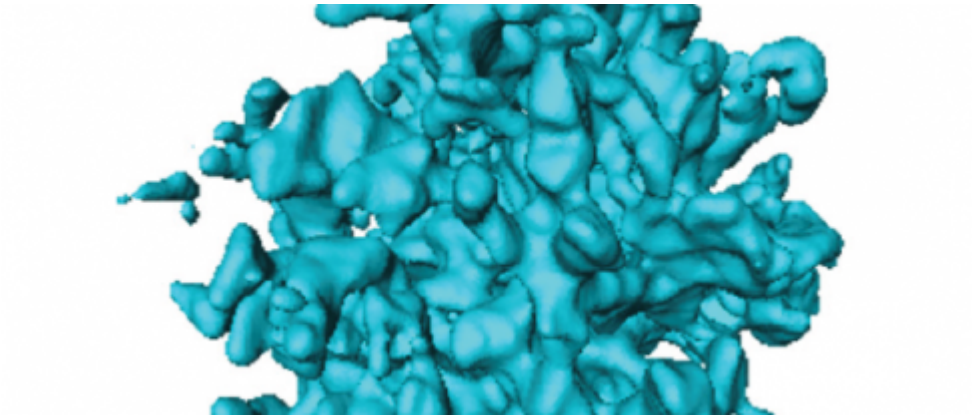

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Loss of selectivity in Fischer-Tropsch synthesis: a high-throughput study

The increase in the level of atmoshpheric CO_2 and the resulting climate change are a global concern. Despite this, the use of fossil fuels continues to grow, in response to high energy demand. Combined with storage and CO_2 conversion solutions, Chemical Looping Combustion processes (CLC) offer a medium-term solution to reducing the impact of energy production from fossil fuels, or even biomass. Essentially, they allow the generation of a flow of concentrated CO_2 that can be captured, then stored or recovered [1].

To do this, these processes use oxygen carrier materials as a substitute for air in combustion, which are deployed in a high-temperature cyclical process, in which they are reduced by the fuel, then regenerated by oxydation. The repetition of these stages subjects them to significant stress - chemical, mechanical and thermal - which alter their lifespan.

Among these ageing mechanisms, a doctoral research project[a] has examined in greater detail the migration of the active phase observed in oxydation-reduction cycles. Focusing on CuO-based oxygen carrier materials supported on Al_2O_3, the thesis characterised their change in *operando* conditions[b] using a multi-scale and multi-technique approach.

In the first instance, Environmental Transmission Electron Microscopy (E-TEM) made it possible to shed a light on the conversion mechanisms involved in the CuO/Cu active phase at the nanometric scale in reactive conditions [2]. It confirmed a very high mobility of the copper in these two forms: oxide and metallic, and showed evidence of the appearance of sintering phenomena[c] as of 500°C.

Subsequently, in addition to the usual techniques (SEM, XRD in particular), the original contribution of SXTM (Scanning Transmission X-ray Microscopy)[d] made it possible to precisely evaluate the structural and textural changes in the materials at the nanometric scale during oxydation-reduction cycles [3]. After change, a correlation can be observed between the textural properties and the chemical composition of the material's various zones, and in particular the progressive formation of alpha alumina and CuO particles as of the initial copper aluminate ($CuAl_2O_4$) and gamma alumina phases. This is illustrated in the figure, which collates the SEM and STXM images acquired of a material that has undergone 50 redox cycles.

Following these observations, two mechanisms were proposed that would explain the change in the $CuO\text{-}Al_2O_3$ system. On the one hand, they relate to the phenomena of diffusion of copper-based species according to temperature, and on the other, the role of copper in the transition to the ?-Al_2O_3 phase.

Thanks to this improved understanding of the phenomena of the mobility of supported copper-based phases and premature formation of alpha alumina, it will be easier to develop solutions to slow the ageing of materials during their implementation in CLC processes. This paves the way for the design of more stable oxygen carrier materials and the redefinition of their optimal operating conditions.

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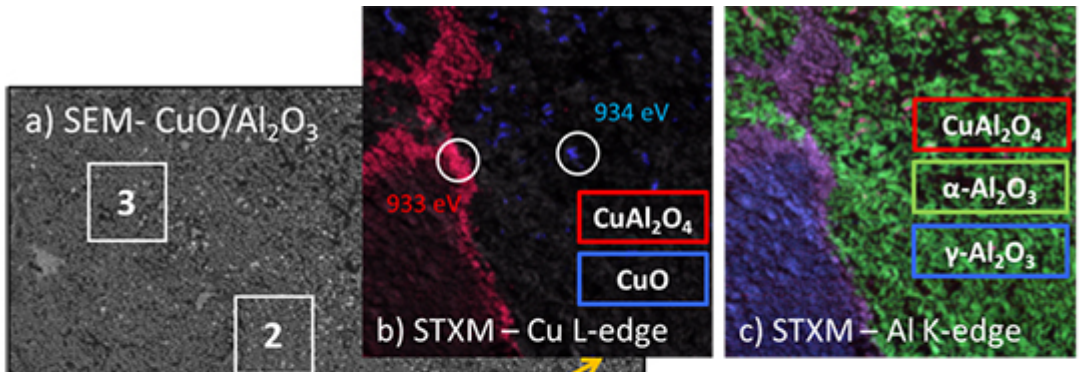

Figure: a) SEM image of a CuO/Al2O3 oxygen carrier material after 50 cycles, and STXM 10x10 ?m mapping of the area indicated by the yellow square; b) at the copper L-edge; c) at the aluminium K-edge.

a- Thesis: « *Understanding the mechanisms leading to copper migration in supported oxygen carrier for Chemical Looping Combustion* », S. Sharna, University of Strasbourg, 2021
b- In representative operating conditions (reactive atmosphere, temperature and pressure)
c- Agglomeration and cohesion of particles when exposed to heat
d- Implementation on the HERMES line of the SOLEIL synchrotron

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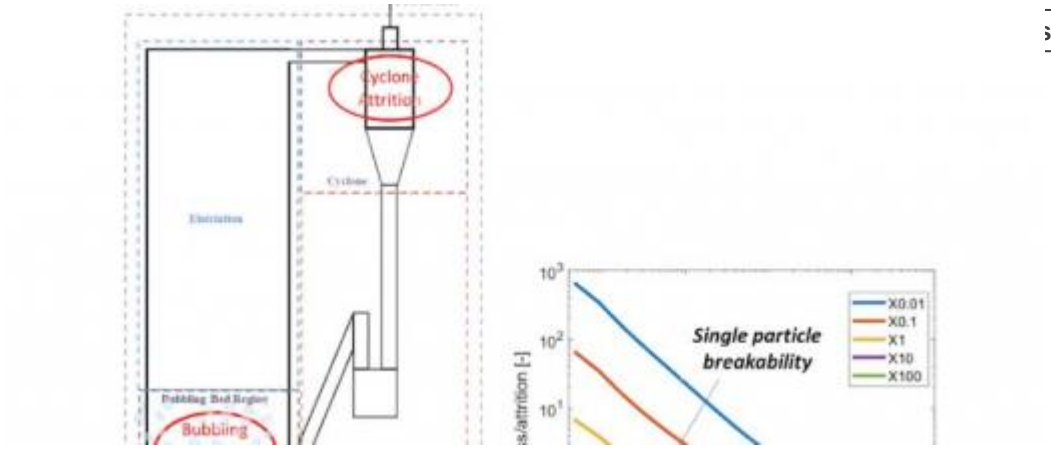

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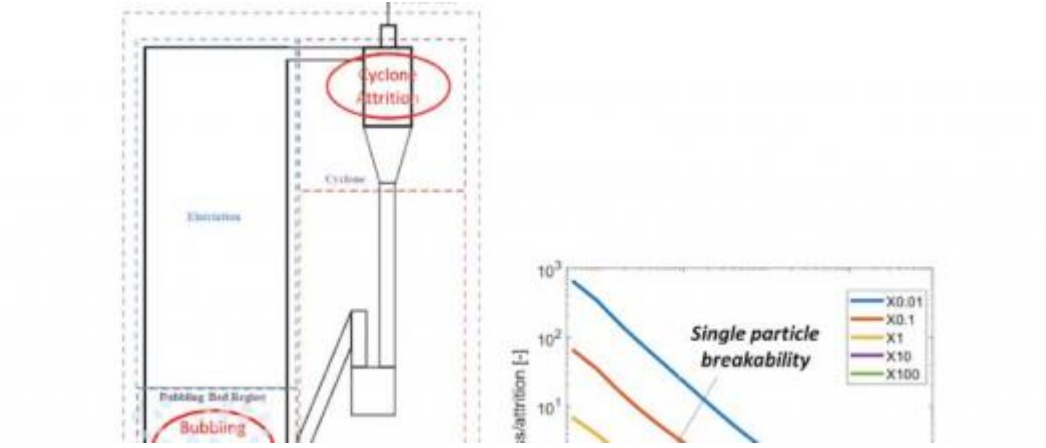

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