Science@ifpen
Issue 19 - December 2014

SPECIAL ISSUE
Young Researchers
Innovative Fuel
Production

To address the major new environmental, economic and social challenges facing the world today, we, as scientists, have a key role to play through the production and use of increasingly advanced knowledge and solutions. Our job is an exciting but demanding one, combining intellectual curiosity, lifelong learning and an open-minded approach, built around method and rigor.

A research scientist's career starts with a PhD thesis: a training experience through research, which, at IFPEN, combines world-class exploratory research with a view to concrete applications. The acquisition of knowledge is essential at this stage – going beyond the main scientific domain in question – in order to encourage creative links between different fields and to pave the way for the future career. It is also an opportunity to unleash initiative, since the doctoral student remains the central player of his research.

This issue, which is dedicated to our young – doctoral and post-doctoral – researchers, illustrates the quality of their contributions to IFPEN's research activity, in the field of innovative fuels production.

We hope that you enjoy this issue,

Hélène Olivier-Bourbigou
Catalysis and Separation Division
2014 Scientific Woman of the Year – Irène Joliot-Curie prize

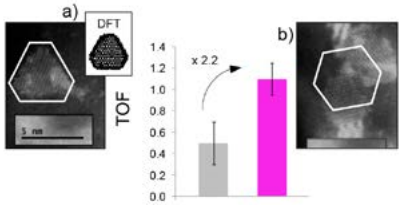
Molecular grafts revive catalysts

The tightening-up of environmental standards is making hydrocracking and hydrotreatment eco-efficient processes a priority for the refining industry and the production of clean fuels.

One of the major levers for improving these processes is increasing the efficiency of the catalysts used: a tungsten dilsulfide phase promoted by nickel (NiWS) supported on amorphous silica-alumina (ASA). However, conventional preparations do not enable sufficient control of genesis of the optimal NiWS active phase, in terms of the number and quality of active sites.

As part of a joint project with ETH Zürich, IFPEN researchers have developed and implemented an innovative catalyst preparation method, inspired by Surface Organometallic Chemistry (SOC), which makes it possible to perform controlled grafting of molecular precursors of tungsten (W) and nickel (Ni) onto the surface of the ASA support. The WS_2 and NiWS phases obtained after sulfurization have demonstrated an unrivalled catalytic activity, due to the presence of nano-crystallites formed at room temperature and regulation of their two-dimensional morphologies. It is through a combination of cutting-edge multitechnical characterizations (NMR, IR, XPS, TEM, HR STEM-HAADF) and *ab initio* quantum calculations that a rational explanation for this unprecedented performance has been uncovered.

Thanks to this research, IFPEN has access to a new methodology for catalyst synthesis, which, in addition to potential industrial-scale applications, is promising for the exploration of other molybdenum-based sulfide catalysts.



Morphology and activity of phases WS_2/ASA phases: a) conventional approach; b) molecular approach.

T. Alphazan, A. Bonduelle-Skrzypczak, C. Legens, A.S. Gay, Z. Boudene, *M. Girleanu, O. Ersen, C. Copéret,* ***P. Raybaud.*** *ACS Catalysis,* 2014. DOI: 10.1021/cs501311m

M. Girleanu, ***T. Alphazan*** *et al. ChemCatChem 6,* 2014, 1594. DOI: 10.1002/cctc.201402115

T. Alphazan *et al.* Patents FR3004967 and FR3004968 (31/10/2014).

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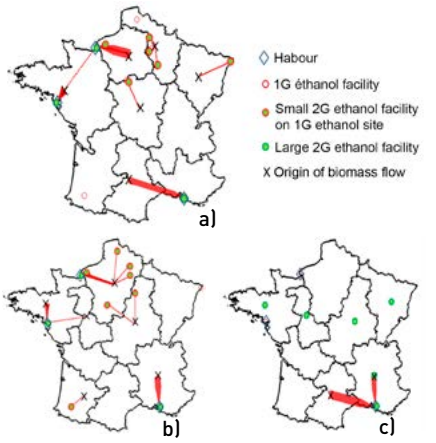
Optimum siting of future biofuel facilities

The emergence of cellulosic biofuel technologies is raising the question of where to locate production units, in terms of the geographic distribution of potential resources, transport infrastructures and other units using biomass energy. In the context of the French project Futurol, prospective modeling studies up to 2030 have led to the creation and analysis of scenarios for the deployment of lignocellulosic ethanol units in France.

Two separate data sets relating to the supply of resources, derived from the AROPAj[1] French agricultural model developed by INRA, have been injected into the MIRET[2] French energy sector model developed by IFPEN. These data, incorporating the availability and average price per region, were derived using two different scenarios based on the assumption of low environmental constraints (scenario a) and high environmental constraints (scenario b). The strategies for siting cellulosic ethanol facilities, and the determining factors, are then based on economic optimization.

Hence it is observed that, depending on scenario (a) or (b), division of the supply basins differs, as do inter-regional flows, but the siting strategies and unit sizes do not. However, on the basis of scenario (b), but using regional wood supply curves (scenario c) rather than availabilities and average prices, the number of cellulosic ethanol facilities and their capacities are radically different.

These spatial modeling approaches demonstrate the importance of the extent of description of resource availability hypotheses and the incorporation of economies of scale in the description of future industrial facilities[3].



Cellulosic ethanol facility spatialization scenarios and biomass flows in 2030:
a) high biomass potential;
b) low biomass potential;
c) low potential with wood supply curves.

(1) *P. Cantelaube, P.-A. Jayet, F. Carre, P. Zakharov and C. Bamps. Land Use Policy, 2012, 29:35-44.*

(2) ***D. Lorne, S. Tchung-Ming.*** *Les cahiers de l'Économie, 2012, n° 87.*

(3) *N. Ben Fradj,* ***D. Lorne,*** *P.-A. Jayet.* Prospective spatial analysis of biomass supply for cellulosic ethanol industry in France. Pending.

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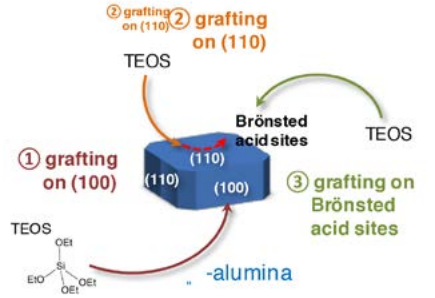
The multiple facets of amorphous aluminosilicates (ASAs)

Amorphous aluminosilicates (ASAs) are strategic materials for use as catalyst supports in the refining industry. Their Brønsted acidity, which is lower than that of crystalline zeolites, makes them ideal for the selective conversion of medium distillates (gas oil and kerosene).

Their multiple synthesis routes produce highly variable structures and surface properties, complicating performance optimization. A model family of ASAs has therefore been developed by grafting molecular precursors onto simple oxide (Si/Al_2O_3 and Al/SiO_2), adjusting the temperature and water content conditions to influence the morphology of the surface mixed phase. Their detailed characterization concerned their acidity and surface properties (*via* catalytic testing and testing of probe molecule adsorption followed by IR spectroscopy and thermogravimetry), along with their structure (by NMR[1] and ToF-SIMS[2]).

The strength of the Brønsted acid sites was accurately assessed by calculation of the turnover frequency[3]: this varies depending on the nature of the ASA, but always remains lower than that of a zeolite. In addition, the acid site environment is much less restricted than for crystalline zeolites. On synthesized deposits in moderate conditions, this study also revealed an original, sequenced and selective mechanism of grafting of the silica precursor to the surface of the alumina.

This new characterization methodology has proved to be applicable to all types of ASAs, particularly industrial ones, paving the way for optimization of their preparation with respect to their catalytic performance.



Sequenced grafting of silica species onto the surface of gamma alumina.

M. Caillot, A. Chaumonnot, M. Digne,
J.A. van Bokhoven. ChemCatChem, 2013, 5, 3644-3656.
DOI: 10.1002/cctc.201300560

M. Caillot, A. Chaumonnot, M. Digne,
J.A. van Bokhoven. J. Catal., 2014, 316, 47-56.
DOI: 10.1016/j.jcat.2014.05.002

1 - Nuclear Magnetic Resonance
2 - Time-of-Flight Secondary Ion Mass Spectroscopy
3 - Parameter reflecting the intrinsic catalytic activity of catalytic sites

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The right catalyst layers go under the microscope

To obtain a lower sulfur content in fuels, despite the use of oils with a high impurity content, significant efficiency improvements need to be made for hydrotreatment and hydrocracking catalysts.

The active phase of these catalysts, tungsten (WS_2) or molybdenum sulfide (MoS_2), are presented in the form of layers, the edges of which host active sites. It is the 2D morphology of the layer that thus determines the type of edge and active sites present. To design new generations of catalysts, it is essential to understand the link between the microstructure at a nanometric – or even atomic – scale and catalytic performance. A fine observation method is therefore required.

Working in collaboration with IPCMS (Strasbourg), which is equipped with cutting-edge equipment (scanning transmission electron microscope, with probe corrector) capable of achieving a resolution of 0.1 nm, IFPEN has developed a method for characterizing the 2D morphology of the layers seen "flat". The originality of this research is that, for the first time, the method has been applied to industrial catalysts, supported on alumina or silica-alumina.

Used to characterize the effect of adding nickel as a promoting agent on the formation of active sites[1], this method has demonstrated the change in morphology – from triangular to hexagonal – of the WS_2 layers supported on silica-alumina. This corroborates molecular modeling results obtained elsewhere.

IFPEN is continuing this research into MoS_2/alumina catalysts, in order to study the effect of active phase synthesis parameters on the 2D morphology of these layers.

(1) *M. Girleanu, **T. Alphazan, Z. Boudene, A. Bonduelle-Skrzypczak, C. Legens, A.S. Gay,** C. Coperet, O. Ersen, **P. Raybaud.** ChemCatChem 2014, 6, 1594-1598*

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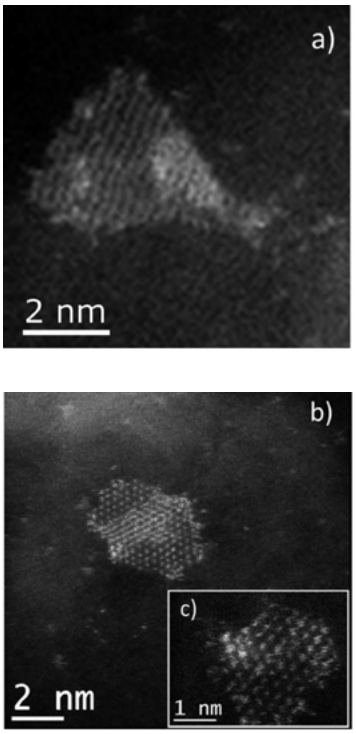


HR HAADF-STEM images of layers of WS_2 and NiWS/amorphous aluminosilicate seen "flat":
a) triangular crystallites of WS_2;
b) truncated triangular crystallites of NiWS;
c) hexagonal crystallites of NiWS.

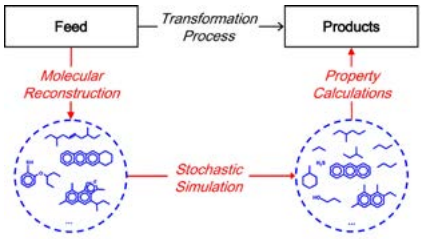
Processes go to Monte Carlo

To address the market demand for light fuels, such as gasoline and gas oil, and given the availability of increasingly heavy crude oils, refiners need to increase the conversion of heavy fractions into valuable products. Designing and optimizing the corresponding processes require detailed models enabling precise prediction of the yields of the output products and their quality.

However, the complexity of distilled oil fractions, in terms of chemical composition and reactivity, as well as the large number of possible reaction pathways, make these processes difficult to model.

To overcome these problems, IFPEN researchers have carried out innovative research employing stochastic approaches to jointly model the composition of the oil fractions and the reactions involved. The "molecular reconstruction" of complex fractions involves replacing them with blends of thousands of molecules that have similar macroscopic properties, as determined by routine analyses. The subsequent process simulation is based on a kinetic Monte Carlo algorithm, applied reaction by reaction. This methodology has been validated on two refining processes.

The originality of this approach lies in the use of molecular-level modeling at every stage of the calculation, both for feedstocks and reactions. The associated advantages are numerous: robustness of the model with respect to feedstock variations, automatic generation of the reaction network, access to the detailed properties of the products without analyses. This approach opens up new opportunities for the simulation of processes using complex feedstocks, particularly biobased feeds.



Stochastic reconstruction and simulation of processes on complex feedstocks.

***L. P. de Oliveira,** A. Trujillo Vazquez, **J.J. Verstraete,** M. Kolb. Energy & Fuels, 2013, 27, 3622-3641. DOI: 10.1021/ef300768u*

***L. P. de Oliveira, J.J Verstraete,** M. Kolb. Catalysis Today, 2014, 220, 208-220. DOI: 10.1016/j.cattod .2013.08.011*

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Towards the in silico formulation of fuels?

Performance, durability, environment and safety considerations dictate that the fuels brought to market need to comply with strict regulations, particularly with respect to their physical chemistry properties (density, viscosity, energetic density, cold flow properties, etc.).

The process of formulating new fuels is innovative and complex due to the growing diversity of the resources used. An innovative method involves the use of QSPR (Quantitative Structure Property Relationship) approaches.

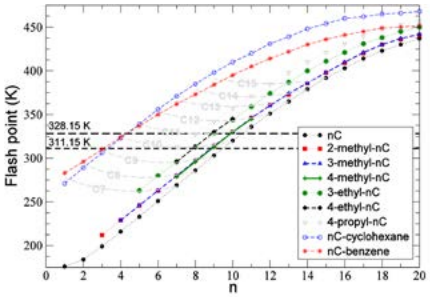
These approaches, which are based on numerical simulation tools, enable the properties of the new compounds to be predicted, as long as reference databases are available. Using the latter, it is possible to rapidly identify formulations to be explored in greater depth.

Still mainly applied to pure substances, these approaches need to be extended to complex blends, in this instance fuels.

The research at IFPEN was conducted in several stages:

- first of all, formating of the experimental data available to build coherent databases;
- then, the development of predictive models, combining different types of molecular descriptions, learning methods and algorithms, statistical approaches, etc.;
- finally, extension of QSPR-type approaches to blends.

The predictive models developed were used to construct tendencies representing different properties. Such example is the flash point of different hydrocarbons. Now successfully extended to complex blends, the QSPR approach offers new opportunities in other fields, for example material-fuel compatibility.



Flash point of hydrocarbons as a function of the number of carbon atoms, adapted from the work of Saldana et al.

D.A. Saldana, B. Creton, P. Mougin, N. Jeuland, B. Rousseau, L. Starck, OGST, 2013, 68, 651. DOI: 10.2516/ogst/2012034

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Innovation

IFPEN ranked among the Top 100 most innovative companies for the 4th time

*IFPEN has earned a place in Thomson Reuters' list of **Top 100 Global Innovators** for the 4th year running. Four French companies and two other research centers (CNRS and CEA) have also been singled out, making France the 3rd most innovative country, behind the USA and Japan. The innovative capacity of companies is assessed on the basis of four parameters: the number of patents filed, patent-filing success rate, the international scope of the patents and, finally, the number of citations by other patents.*

IFPEN thesis prize

*The annual IFPEN thesis prize/2014 Yves Chauvin prize was awarded to **Thibault Alphazan** for his research entitled "Towards the molecular design of hydrotreatment catalysts prepared from metal-organic precursors" (20 November 2014).*

Upcoming scientific events

- *IFP Energies nouvelles' "Rencontres scientifiques" event – **LowPerm2015** – 9-11 June 2015, IFPEN Rueil-Malmaison - www.rs-lowperm2015.com*
- *IFP Energies nouvelles' "Rencontres scientifiques" event – **Microfluidics** – 4-5 November 2015, IFPEN Rueil-Malmaison - www.rs-microfluidics2015.com*
- *IFP Energies nouvelles' "Rencontres scientifiques" event – **SimRace** – 8-10 December 2015, IFPEN Rueil-Malmaison - www.rs-simrace.com*

HDR

- ***Frédéric Augier,** HDR at the École Centrale de Lyon: "Modeling of closely coupled phenomena with a view to scale change" (September 2014).*

Publications

- *"IFPEN's "Innovation news": special edition on "Scientific hurdles" (November 2014)*

Awards

Hélène Olivier-Bourbigou, Scientific Woman of the Year

The 2014 Irène Joliot-Curie prize, in the Scientific Woman of the Year category, was awarded to Hélène Olivier-Bourbigou, Department Head within IFPEN's Catalysis and Separation Division. This prize recognizes the work carried out by Hélène Olivier-Bourbigou in the field of homogeneous catalysis. For the past 25 years, her research has been contributing to the global reputation and international influence of French catalysis. Her work forms a natural continuum following on from the research conducted by Yves Chauvin, winner of the 2005 Nobel prize in Chemistry, who supervised her doctoral thesis. She was given the prize at an official ceremony chaired by the French Minister for Higher Education and Research on 18 November.

Managing Editor: Marco De Michelis
Editor-in-chief: Éric Heintzé
Editorial committee: Xavier Longaygue, Laurent Forti, Françoise Brucy
Graphic Design: Esquif
ISSN No. 1957-3537

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