



Science@ifpen

Issue 25 - July 2016



Catalysis and separation are essential fields when it comes to conceiving environmentally-friendly innovations in the energy and chemistry sectors. By combining catalytic and separation steps, innovative, more energy-efficient processes can be developed, with better yields and limiting the production of by-products. This has a major impact given that over 80% of the products we use today have undergone one or more of these steps during their manufacturing process!

Drawing on its expertise and advanced methodologies, combining high-throughput experimentation with molecular modeling, IFPEN has established itself as an internationally recognized player in the design of differentiated catalytic and/or separation solutions. For example, it is now one of the world leaders for publications and patents in the field of sulfide catalysis, metal catalysis, acid-base catalysis and molecular catalysis. It is also actively involved in the development of new sectors, such as biofuels, bio-based chemistry, or CO₂ conversion.

Its broad influence is illustrated here by a few studies published recently in liaison with academia.

I hope you enjoy reading this issue.

Denis Guillaume
Director of the Catalysis and Separation Division

Zeolite based adsorbents and xylene separation: cracking the combination

IFPEN has been developing adsorbents based on faujasite zeolite for a number of years already for its Eluxyl® process for the separation of xylenes used in the manufacture of PET resin^a. But, despite the numerous studies conducted in this field, the origin of the selectivity of xylene isomers in these zeolites had remained unclear until now.

However, this has recently changed, thanks to a new combinatorial experimental strategy implemented in collaboration with IRCELYon⁽¹⁾, using HTE^b, combined with statistical analysis of the adsorption data obtained. The method is based on the construction of structure-property correlative statistical models^c, an approach that has rarely been applied in the field of materials for separation by adsorption.

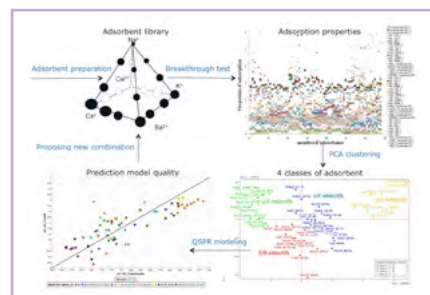
A library of 70 adsorbents was compiled, with these then being tested using dedicated, automated, parallel experimental systems.

A statistical analysis of the results was performed, focusing on both the adsorption properties — demonstrating the existence of different adsorbent classes⁽²⁾ — and the descriptors of the solids tested, thus making it possible to select the most pertinent ones.

The descriptors selected for the correlative model between structure and adsorption properties primarily characterize the confinement status of the molecules inside

the faujasite zeolite. During adsorption, this confinement can give certain molecules more favorable configurations, thereby explaining the entropic nature of the selectivity inside this material.

By improving our understanding of the materials explored and helping, theoretically, to target the best structures, this combinatorial experimental strategy will contribute to the discovery of new adsorbents, optimized for the application in question. ■



Combinatorial experimental strategy for the discovery of new adsorbents.

- a - Polyethylene Terephthalate
- b - High-Throughput Experimentation
- c - Quantitative Structure-Properties Relationship (QSPR) models

(1) Y. Khabzina, UCBL doctoral thesis, 2015.

(2) Y. Khabzina, C. Laroche, J. Perez Pellitero, D. Farrusseng, submitted to *Microporous and Mesoporous Materials*.

Scientific contact:
catherine.laroche@ifpen.fr

IFP Energies nouvelles (IFPEN) is a major research and training player in the fields of energy, transport and the environment. From research to industry, technological innovation is central to all its activities.



Quantum chemistry sheds light on catalytic mechanisms

To improve the activity of a catalyst, it is essential to elucidate the reaction mechanisms on a molecular scale. In the field of heterogeneous catalysis, this is a complex procedure requiring the use of methodologies combining experiments and modeling on various scales.

IFPEN and the Surface Reactivity Laboratory at Pierre et Marie Curie University (UPMC) have implemented this approach in the dehydration of a bio-based alcohol on an alumina-based catalyst (γ - Al_2O_3). By combining *ab initio* calculations^a, kinetic modeling and experimental measurements, the mechanism and rate of each reaction step have been described from molecular to reactor scale^[1,2].

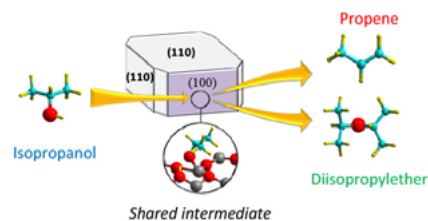
Hence, by successive iterations, it has been possible to obtain consolidated kinetic models, associated with a description of the reaction paths, so that macroscopic

features and molecular-scale behavior can now be linked.

This approach has demonstrated that, in the conditions used, the crystallographic surface (100) of gamma alumina was the only active one. It has also shown that a very specific combination of a reactive alumina site and two connected sites (an oxygen atom and a second aluminum atom) is the source of all the products formed (alkene, ether, water).

The effect on the selectivity of the catalyst of the species adsorbed (water, alcohol) around the active site has also been observed.

In practice, the information uncovered paves the way for improving the activity of alumina *via* synthetic processes aimed at increasing the surface area proportion of the (100) surfaces. ■



Scheme of dehydration of alcohols on γ -alumina determined by DFT.

[1] K. Larmier, C. Chizallet, N. Cadran, S. Maury, J. Abboud, A-F. Lamic-Humblot, E. Marceau, H. Lauron-Pernot, *ACS Catalysis*, 2015, 5, 4423-4437. DOI: 10.1021/acscatal.5b00723

[2] K. Larmier, A. Nicolle, C. Chizallet, N. Cadran, S. Maury, A-F. Lamic-Humblot, E. Marceau, H. Lauron-Pernot, *ACS Catalysis*, 2016, 6, 1905-1920. DOI: 10.1021/acscatal.6b00080

a - Calculations based on quantum chemistry

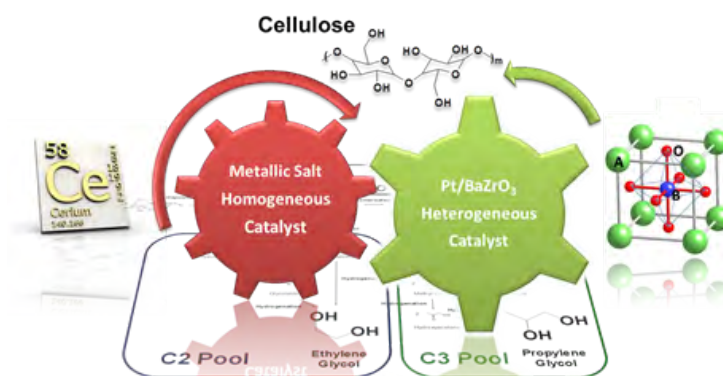
Scientific contact:
celine.chizallet@ifpen.fr

A catalytic combination for bio-based plastics

The use of an abundant renewable resource, such as lignocellulosic biomass, represents a significant opportunity for the production of major fine chemical intermediates, as an alternative to current petro-based processes. One of the main objectives of this bio-based process is to obtain glycols, such as the ethylene glycol used in bio-based grade plastics.

The wealth of chemical functions contained in the cellulose of biomass is undoubtedly an advantage to produce a broad diversity of molecules, but it is also a source of difficulty to achieve high levels of selectivity. Specific multifunctional, active and stable catalytic systems must therefore be specially designed to efficiently produce bioglycols.

For the past few years, IFPEN has been working in this area, applying an innovative dual catalysis approach, combining homogeneous and heterogeneous catalysts. Coupled with an in-depth knowledge of the possible reaction pathways, the flexibility related to this combination of catalysis operations, and the diversity of the catalytic functions involved, make it possible to improve the selectivity of the transformation to glycols^[1]. For example, when cerium chloride (CeCl_3) is associated with a



Production of ethylene and propylene glycol by dual catalysis from cellulose.

heterogeneous catalyst containing platinum deposited on basic support (such as cerium oxide or perovskite), the cellulose conversion was complete and selectivity to ethylene glycol is multiplied 7-fold compared to a test in the presence of a single heterogeneous catalyst^[2].

The discovery of brand new catalytic systems using this original approach is contributing to IFPEN innovations in the conversion of biomass into products of interest, a key theme in the field of chemistry serving a low-carbon economy.

The research is ongoing, with the optimization of these new multifunctional

catalytic systems in order to expand the range of resources that can be transformed from cellulosic biomass to more simple sugars, such as glucose. ■

[1] E. Girard, D. Delcroix, A. Cabiac, patent applications FR 14/53.426, 14/53.425

[2] E. Girard, D. Delcroix, A. Cabiac, *Catal. Sci. Tech.*, 2016, 6, 5534-5542. DOI: 10.1039/C5CY01782C

Scientific contacts:
amandine.cabiac@ifpen.fr
damien.delcroix@ifpen.fr

Cracking heavy crudes

To convert and use ever more complex crude oils, it is necessary to refine increasingly heavy oil cuts into lighter products (medium distillates). Hydrocracking (HCK) is a key process that can be used to address this problem. The associated catalysts therefore need to be ever more selective, while still maintaining high activities.

Two research strategies have been put in place to increase the selectivity of HCK catalysts, in particular working on the intrinsic properties of the acid supports used.

Firstly, two innovative families of zeolite Y nanocrystals have been developed, presenting crystallite sizes of 40 and 380 nm, much smaller than conventional particles^[1]. The expected increase in selectivity would result from lower diffusional limitation of the reagents and products of the catalyzed reaction.

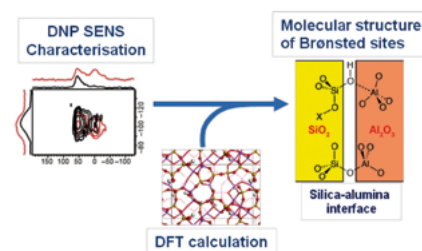
In addition, to enable control of acidity, the factors governing it on mesoporous

amorphous aluminosilicate (ASA) supports have been explained. This has been achieved by combining three approaches to correlate surface structure and acidity:

- the synthesis of model ASAs,
- molecular modeling proposing an atomical description of the Brønsted acid sites^a,
- DNP-SENS analyses^b, conducted at the European Center for High Field NMR (CRMN) in collaboration with ETH Zürich, to more precisely determine the nature of the acid sites proposed^{d[2]}.

This promising research paves the way for the design of optimized acidic solids and guides future developments for the creation of innovative catalysts using these same solids. ■

- a - Site capable to donate H⁺ (protons)
- b - Dynamic Nuclear Polarization Surface Enhanced NMR Spectroscopy
- c - Using Density Functional Theory (DFT)



"Surface state/acid site" description of ASAs by combined DNP-SENS and DFT^c.

[1] M. Dodin, N. Bats, E. Guillon, patent 2015 No. 15/50.149

[2] M. Valla, A. J. Rossini, M. Caillot, C. Chizallet, P. Raybaud, A. Chaumonnot, M. Digne, A. Lesage, L. Emsley, J. A. van Bokhoven, C. Copéret, *J. Am. Chem. Soc.*, 2015, 137, 33, 10710. DOI: 10.1021/jacs.5b06134

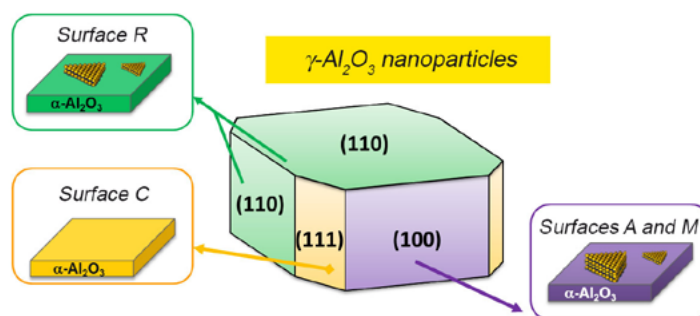
Scientific contacts:
alexandra.chaumonnot@ifpen.fr
celine.chizallet@ifpen.fr

Effective fuel desulfurization: a question of orientation

Hydrotreatment catalysts are used to reduce the sulfur content of fuels. They are based on MoS₂, promoted by cobalt or nickel, and supported on an oxide, such as γ -alumina. The support has a significant influence on the structure of the active phase. However, this role had never been completely elucidated.

IFPEN and the Surface Reactivity Laboratory at UPMC have developed an original approach, based on the science of surfaces for heterogeneous catalysis, the aim being to study the specific role of four crystalline surfaces of a model alumina (α -alumina). This research has demonstrated that the reactivity of the different crystallographic planes (called A, M, C and R) with respect to the adsorption of molybdenum is controlled by the speciation of surface hydroxyls, which determines the surface charges at the water/oxide support interface during the metal impregnation phase.

It has thus been shown that the C surface is inert and that the R plane has a limited adsorption capacity, while A and M surfaces are highly reactive with respect to the adsorption of molybdenum.



Analogy between α -alumina and γ -alumina surfaces.

Following the sulfurization of these solids, A and M surfaces present the highest sulfurization rates. Conversely, a low sulfurization rate is obtained on surface R.

The structural analogy between α and γ alumina has made it possible to extend these results to industrial catalysts, for which it has been established that molybdenum dispersion and sulfurization rate are dependent on the crystallographic orientation of the oxide support surface.

This new knowledge paves the way for progress in the development of

hydrotreatment catalysts *via* adequate control of γ -alumina morphology. ■

C. Bara, L. Plais, K. Larmier, E. Devers, M. Digne, A-F. Lamic-Humblot, G. Pirngruber, X. Carrier, *J. Am. Chem. Soc.*, 2015, 137, 15915–15928. DOI: 10.1021/jacs.5b10975

C. Bara, E. Devers, M. Digne, A-F. Lamic-Humblot, G. Pirngruber, X. Carrier, *ChemCatChem*, 2015, 7, 3422–3440. DOI: 10.1002/cctc.201500436

Scientific contact:
elodie.devers@ifpen.fr

Fischer-Tropsch: a synthesis process that's still green

Fischer-Tropsch (FT) synthesis is a catalytic process for the production of hydrocarbons based on carbon monoxide hydrogenation. It still poses a number of challenges in terms of catalyst optimization due to the complexity of the phenomena that occur on the surface of the active phase particles. Obtaining liquid hydrocarbons from a synthetic gas, produced from natural gas or biomass, is an interesting option, however, in order to reduce the share of oil in the energy mix.

It is for this reason that IFPEN is focusing on Fischer-Tropsch synthesis as part of the BioTfuel multi-partnership demonstration platform.

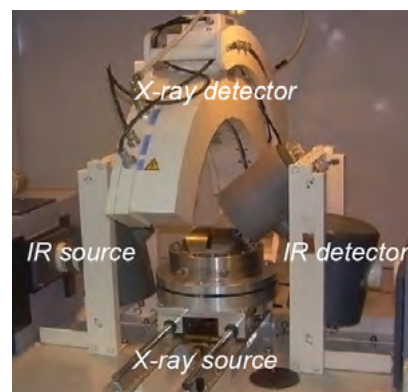


The challenge in terms of improving the properties of the cobalt-based FT synthesis catalyst is related to two factors: the inability to correlate the structure and reactivity of nanometric cobalt particles and to identify, in representative conditions, the mechanism governing the growth of hydrocarbon chains.

An *operando* method combining simultaneous characterization of the catalyst and its properties, in realistic reaction conditions (pressurized), has opened up new avenues at IFPEN. The structure of these solids, their surface and their catalytic properties have thus been characterized by combining different analysis techniques [XRD^a, DRIFTS^b and GC^c]⁽¹⁾.

In addition, working in collaboration with IRCE Lyon⁽²⁾, the SSITKA analysis technique^d has made it possible to better characterize the relationship between structure and carbon chain formation mechanism. This work has also led to the identification of two types of specific sites which, thanks to an original microkinetic model, have been linked to the overall properties of the active phase. ■

a - X-ray Diffraction
b - Diffuse Reflection Infrared Spectroscopy
c - Gas Chromatography
d - Steady State Isotopic Transient Kinetic Analysis



Combined operando XRD-DRIFTS analytical technique.

(1) J. Scalbert, I. Cléménçon, P. Lecour, L. Braconnier, F. Diehl, C. Legens, *Catal. Sci. Technol.*, 2015.
DOI: 10.1039/c5cy00556f

(2) E. Rebmann, P. Fongarland, V. Lecocq, F. Diehl, Y. Schuurman, *Catalysis Today*.
DOI:10.1016/j.cattod.2015.11.041

Scientific contacts:
christelle.legens@ifpen.fr
fabrice.diehl@ifpen.fr

News

In 2015, IFPEN maintained its 13th place in the French National Industrial Property (INPI) rankings of patent filers in France. Of 182 patents filed, 97 related to New Energy Technologies (NETs).

Appointment

• **Grégoire Allaire** has been appointed Chairman of IFPEN's Scientific Board. He takes over from Sébastien Candel, whose mandate has come to an end. Grégoire Allaire is Professor of Applied Mathematics at the École Polytechnique.

Publications

• OGST – IFP Energies nouvelles journal – Issue 2, volume 71 (2016). Special Yves Chauvin tribute issue. <http://ogst.ifpenouvelles.fr>

• CVT Ancre – Study on the development of deep underground. www.allianceenergie.fr/

Awards

• **Malika Boualleg** was awarded the 2016 prize from the Analytical Chemistry Division of the French Chemistry Society (SCF) on 26 May for her project team's research focusing on the development of a selective lithium adsorbent. Her work has contributed to the identification of new alumina concepts for catalytic systems in the field of refining and petrochemicals.

• **Bruno Miguel Da Silva Pinho**, a former IFPEN PhD student, was awarded the International Society for Advancement of Supercritical Fluids (ISASF) thesis prize in May for his innovative research concerning C₃ hydrogenation in supercritical medium.

• **Zoé Buniazet**, a PhD student at IFPEN, was awarded the Young Scientist award at the 16th International Congress on Catalysis 2016 (Beijing, China), for her research concerning the dehydration of bioalcohols, an alternative process for the production of non-fossil olefins.

Upcoming scientific events

• IFP Energies nouvelles' "Rencontres scientifiques" event – **DEFI: flow dynamics at fluid interfaces – Collection of physicochemical and rheological properties** – 12-13 October 2016, IFPEN-Lyon - www.rs-defi2016.com

• IFP Energies nouvelles' "Rencontres scientifiques" event – **LES4ICE 2016: Large-Eddy Simulation for flows in internal combustion engines** – 30 November and 1 December 2016, IFPEN Rueil-Malmaison - www.rs-les4ice.com

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

To get in touch with IFPEN or receive Science@ifpen:
Institutional Relations and Communications Division:
Tel: +33 1 47 52 51 34 - Science@ifpen.fr
1 et 4, avenue de Bois-Préau - 92852 Rueil-Malmaison Cedex - France
Press contact: A.-L. de Marignan - Tel: +33 1 47 52 62 07