

# Surface and Interfacial Chemistry

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**Abstract:** Based on a molecular approach combining controlled surface chemistry, advanced spectroscopic methods, in particular solid-state NMR, and computational chemistry, it is possible to develop single-site species and to control the growth of nanoparticles on supports. This allows the generation of highly efficient catalysts combining the advantages of both homogeneous and heterogeneous catalysts and function materials with defined properties.

**Keywords:** Functional materials · Nanoparticles · Oxides · Spectroscopy · Surface



**Christophe Copéret** obtained the equivalent of a Master degree in Chemistry and Chemical Engineering from CPE Lyon in 1992, before carrying out a PhD with Prof. Negishi (Purdue University, 1996). After a post-doctoral research stay with Prof. Sharpless (Scripps, 1997), CCH accepted a research position at CNRS (LCOMS – CPE Lyon, 1998). In 2008, he was promoted CNRS research director and in 2010, he moved to ETH Zürich (Institute of Inorganic Chemistry). His scientific interest lies at the frontiers of molecular, material and surface chemistry, with the aim to design functional materials with applications in catalysis (sustainable chemistry and energy), molecular recognition, imaging and microelectronics. Besides scientific activities, CCH enjoys literature, history, cooking and wine tasting, probably a reminiscence of his childhood spent in the vineyards of Fleurie, one of the famous *crû* of Beaujolais – La Reine – just 50 km north of Lyon.

## 1. Background, Motivation and Strategy

Bridging the gap between homogeneous and heterogeneous catalysis has been our playground for the last fourteen years, trying to use molecular approaches to design and understand heterogeneous catalysts.<sup>[1]</sup> This research topic stems from the fact that heterogeneous catalysts typically suffer from a lack of understanding of the structure of their active sites – preventing the use of structure–reactivity approach towards their improvements – while they offer great advantages in terms of chemical processes (separation, recycling and regeneration of the catalyst) over homogeneous catalysts.

Our research effort has thus focused on generating well-defined sites at the surface of materials and at characterizing them at the molecular level, so that structure–reactivity relationships could be drawn and more rational development implemented as is typically performed in homogeneous catalysis. This combined with a computational approach allows refining structures, understanding their spectroscopic signatures and reactivity to *in fine* generating more predictive models and lead-structures for rational design of catalysts. Obviously, this approach/methodology is certainly not restricted to the conception of heterogeneous catalysts, which are essential to develop sustainable chemistry and tackle energy and environmental problems, but it also opens new avenues to design functional materials at the molecular level where surfaces and surface interactions are key to their properties, for instance in bio-probe for imaging, sensing technologies, gas purification and storage, electronic applications to name but a few.

Overall an approach relying on structure–property relationship implies control of the surface chemistry of materials and detailed characterization of surface species. In the following section, we thus

describe the methods employed and developed in our laboratory to understand surfaces at a molecular level, to control site density towards ‘single-site’ species, to introduce diversity in oxide solids, and to control the growth of nanoparticles on supports.

## 2. Understanding Surfaces at a Molecular Level: Tools

If one wants to control the chemistry at the surface of materials, it is necessary to obtain a detailed understanding of the surface functionality (type and density); this obviously requires the use and development of advanced spectroscopic methods in order to refine the structure of surface species as well as the bulk of the solid. This implies using surface science as well as solid-state structural investigation techniques, but also utilizing and transposing the spectroscopic methods of molecular chemistry to surface chemistry. Transmission or scanning electron microscopy (TEM and SEM) in combination with N<sub>2</sub> adsorption or chemisorption experiments give very important information about the texture, the shape, and the size of the materials. X-ray crystallography is also an essential tool to understand the structure of solids. While ideal to characterize the bulk of crystalline materials, it requires periodicity and is thus rarely applicable to surface chemistry. It can be replaced by XANES and EXAFS, which provide critical information about the oxidation state, the geometry and the coordination sphere of the surface sites (distance, geometry and number of neighbors). This can be complemented by UV-Vis spectroscopy and surface science techniques (XPS, Auger). Vibrational spectroscopy (IR and Raman) is also a very powerful tool giving critical information about surface functionalities and their density; it is particularly useful to monitor chemical transformation of sur-

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face functional groups. In molecular chemistry however, one of the most powerful methods to probe local structure, environment and dynamics is clearly NMR (and EPR) spectroscopy. In surface chemistry, NMR mainly suffers from the low concentration of surface species combined with the inherent low sensitivity of the methods (this is not the case for EPR). This has been however circumvented by labeling the sample or by using methods to selectively enhance the signals of surface species such as polarization techniques (relying on i) abundant nuclei, typically protons, ii) Xe, or iii) more recently electrons in a technique named Surface Enhanced NMR).<sup>[2-7]</sup> Of these methods, we try to exploit in particular the NMR signatures of surface sites to understand their structure and dynamics.<sup>[8]</sup> This involves studying directly the ligands attached to the metal sites, using probe molecules such as  $N_2$ ,  $H_2$ ,  $CH_4$ , CO or  $PMe_3$  or even reactants in order to trap reaction intermediates.<sup>[9]</sup> Spectroscopic investigations are best carried out when combined with computational chemistry in order to assign spectroscopic signatures to specific surface species.

Overall, these techniques/tools are critical to provide very detailed information allowing surface structures to be characterized at the molecular level. Thus our group uses and/or develops these techniques, typically in close collaboration with experts in the field; this is particularly the case for NMR spectroscopy and computational chemistry.

### 3. Controlling Site Density towards 'Single-site' Species: Method I

Heterogeneous catalysts are typically composed of a support, which is very often an oxide such as silica, alumina or aluminosilicates. In view of controlling active site density and generating supported single-site catalysts, it is thus of prime importance to understand the surface composition of the support and to control the types and the densities of surface functionalities.<sup>[10]</sup>

For oxides of general formula  $E_xO_y$ , the surface presents E-O-E and E-OH terminations, whose types and densities can be modulated by thermal pre-treatment under vacuum or a gas flow.

For instance, silica nanoparticles can be treated up to 700–800 °C without significant loss of surface area, and the OH density decreases almost exponentially between 200 and 800 °C by condensation of neighboring OH groups with production of  $H_2O$  and siloxane bridges of increasing strain (Fig. 1a). At 700 °C, a surface coverage of ca. 1 OH.nm<sup>-2</sup> is obtained, where the OH groups are mostly isolated and present a sharp signal in the IR spectrum at 3747

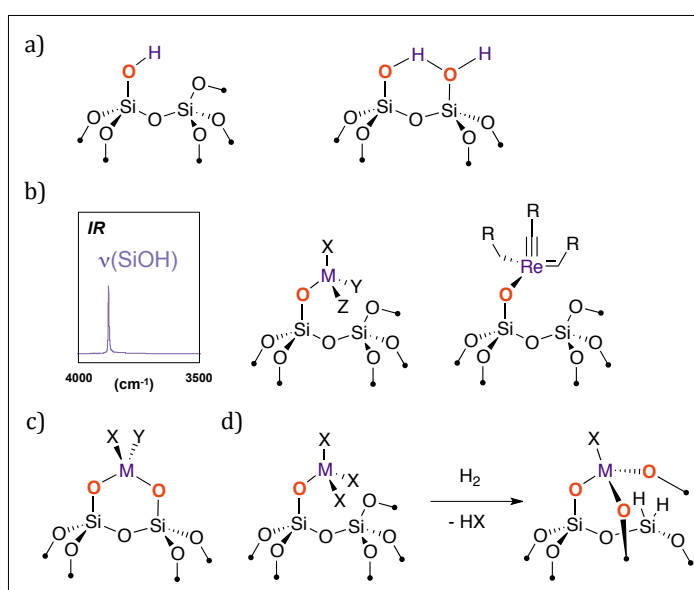


Fig. 1. a) Major OH terminations for silica surfaces. b) IR spectrum of a silica partially dehydroxylated at 700 °C composed of mainly isolated silanols – the resulting general structure for tetracoordinated mono-grafted species and the example of a Re surface complex. c) Idealized bis-grafted species usually obtained as major species on silica partially dehydroxylated at 200 °C. d) Conversion under H<sub>2</sub> of mono-grafted species into tris-grafted species *via* opening of adjacent siloxane bridges.

cm<sup>-1</sup>. By and large, metal complexes react with these isolated surface silanols *via* replacement of one M–X by a M–OSi ligand (Fig. 1b). This yields well-defined and site isolated surface species mono-grafted to silica,<sup>[10]</sup> which display catalytic performances often greater than their homogeneous counterpart, *e.g.* in alkene metathesis.<sup>[11]</sup> Additionally, using lower thermal treatment for silica and thus increasing silanol density provides a way to generated surface species multiply grafted – usually

bis-grafted – to the support (Fig. 1c), thus increasing its stability.<sup>[10]</sup> This can also be achieved by post-thermal treatment, typically in the presence of H<sub>2</sub>, of grafted species, which, upon reaction with adjacent siloxane bridges, are transformed in multiply bonded species (Fig. 1d).

Similarly, the OH density of  $\gamma$ -alumina can be controlled *via* partial dehydroxylation under vacuum, but here the surface chemistry is more complex since there are different types of OH groups and since

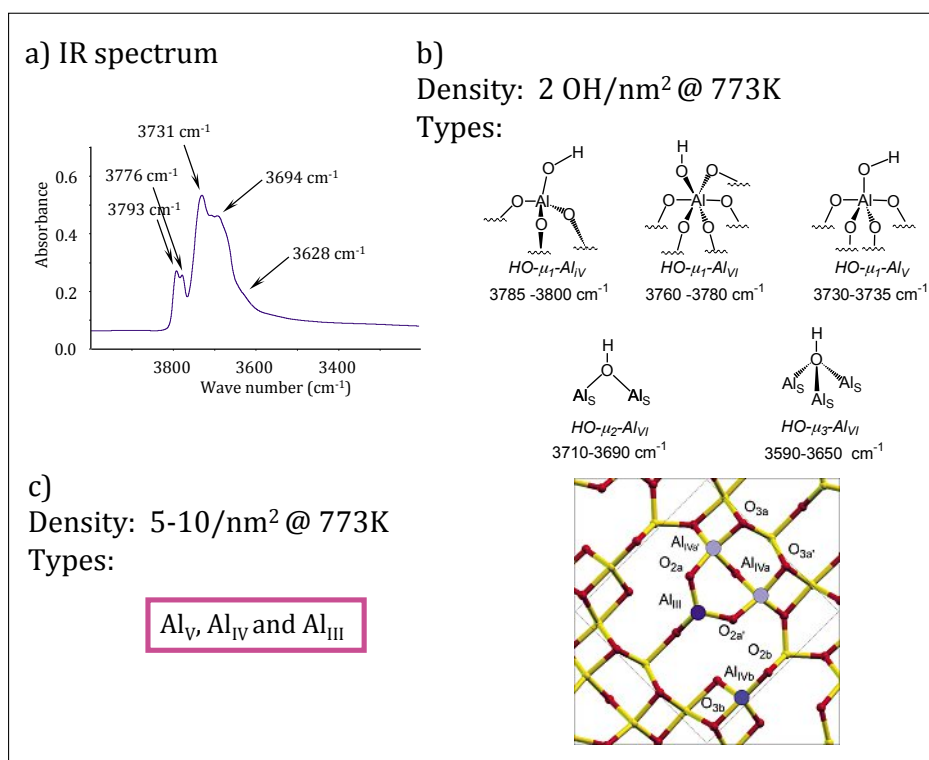
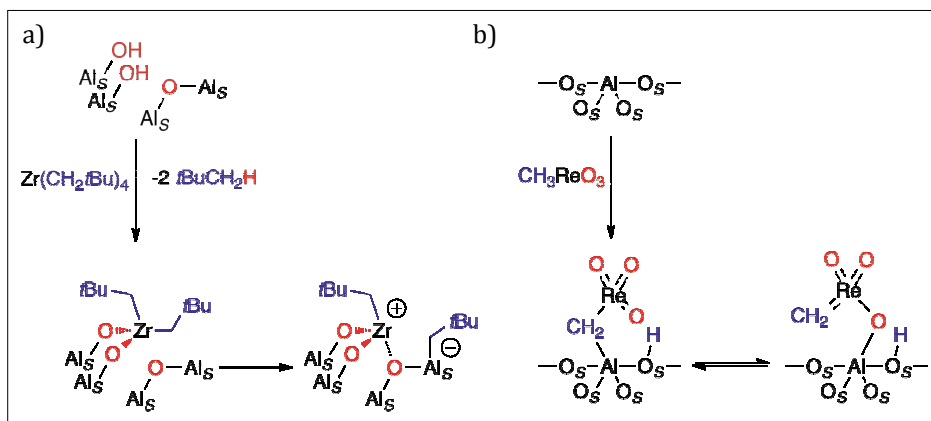


Fig. 2. a) IR spectrum of the OH region of a  $\gamma$ -alumina partially dehydroxylated at 500 °C. b) Density and types of hydroxyl groups. c) Density of Lewis acid sites and their idealized structure illustrated using a fully dehydroxylated 110 facet of  $\gamma$ -alumina.



Scheme 1. Grafting on  $\gamma$ - $\text{Al}_2\text{O}_3$  partially dehydroxylated at 500 °C: a) tetrakis(neopentyl)zirconium and b) methyltrioxorhenium.

Lewis acid sites are exposed upon thermal treatment (Fig. 2). This results from the presence of tetrahedral and octahedral sites in the bulk of  $\gamma$ -alumina (1:3 ratio of Td and Oh). Through detailed investigations combining spectroscopic methods and computational chemistry, the IR signatures of each type of OH groups can be identified. Moreover, we have shown that the structure of the so-called defect sites of  $\gamma$ -alumina corresponds to tri-coordinated Al sites ( $\text{Al}_{\text{III}}$ ), which are at the same time stabilized and activated by water! Water stabilizes the 110 termination that exposes the  $\text{Al}_{\text{III}}$  sites and increases the Lewis basicity of adjacent O atoms without affecting the Lewis acidity of  $\text{Al}_{\text{III}}$  site at low water coverage, thus providing a highly reactive  $\text{Al}_2\text{O}$  frustrated ion pair. This explains the high reactivity of partially dehydroxylated alumina towards small molecules like  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{N}_2$ .<sup>[10,12–14]</sup>

It also explains the formation of highly reactive surface species. For instance, grafting alkyl zirconium derivatives such as  $[(\text{tBuCH}_2)_4\text{Zr}]$  generates cationic intermediates, which are highly active polymerization catalysts (Scheme 1a).<sup>[15]</sup> In a different way  $\text{CH}_3\text{ReO}_3$  is activated upon adsorption on  $\gamma$ -alumina, through the C–H bond activation of the methyl ligand, which generate a  $\mu^2$ -methylene species, which corresponds to the resting state of a highly active alkene metathesis catalyst (Scheme 1b).<sup>[16,17]</sup>

These examples clearly illustrate our approach, and the critical need to understand surface structures of metal oxides as a first step towards the generation and the design of highly active catalysts. Therefore, our group invests major research efforts towards the molecular understanding of metal oxides, thus allowing design of well-defined metal sites. We have mainly focused so far on generating single-site catalysts, but we have also shown that this principle can be used to tune the luminescence of silica nanoparticles.<sup>[18]</sup>

This has led us over the years to de-

velop a technological platform to tackle this question: it involves the synthesis of molecular precursors and materials, high-vacuum techniques to prepare the surface of materials (clean surface with controlled site density), chemisorption methods to understand the texture of materials and their reactivity, *in situ* spectroscopic methods and advanced NMR techniques (*vide supra*).

#### 4. Introducing Diversity in Oxide Surfaces: Method II

In view of the plethora of ligands in transition-metal chemistry and their dramatic impact on the reactivity and the property of the transition-metal ion, oxide

surfaces can be viewed as rather limited as they can mainly provide O-terminated ligands. With the idea of conserving the beneficial effect of site isolation and molecular control, one of our research interests has been to generate materials with perfectly distributed organic functionalities at the surface of an inorganic matrix like silica. Such materials have been developed in the past few years through the synthesis of meso-structured hybrid organic–inorganic materials. Prepared in the presence of a structure-directing agent, a surfactant, allows the regular distribution of the organic functionalities in the pore or even the wall of the solid.<sup>[19]</sup> Our contribution has been to selectively link organometallics on these organic functionalities while generating an unreactive surface through typically passivation of the surface silanols. This powerful approach provides well-defined metal centers attached to the support by a strong M–ligand bond. This has led to the preparation of immobilized catalysts combining the catalytic performance of their homogeneous analogues and the possibility of recycling of heterogeneous catalysts. We have so far developed catalysts for the C–H bond functionalization, the metathesis of alkenes, and the hydrogenation of  $\text{CO}_2$  (Fig. 3).<sup>[20–22]</sup> This promising approach is clearly applicable to a broad range of ligands so that most – if not all – homogeneous catalysts can be made heterogeneous and so that the development of functional materials for various applications is possible.

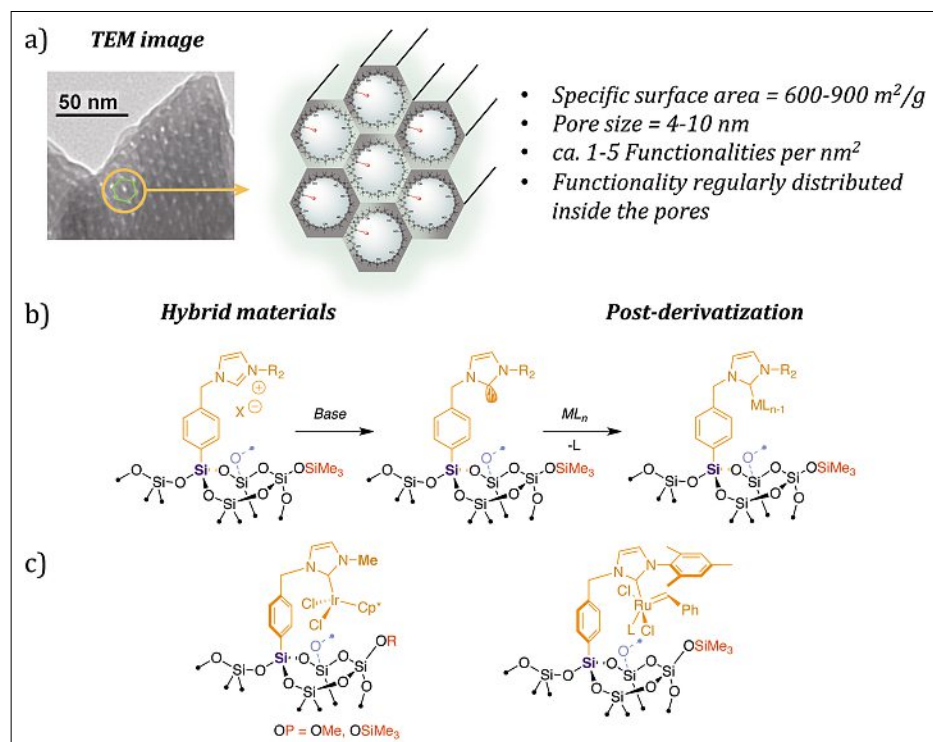


Fig. 3. a) Generality on hybrid materials. b) Approach to generate catalysts from imidazolium functionalities. c) Examples of catalysts (Ir for catalytic C–H functionalization and Ru for alkene metathesis).



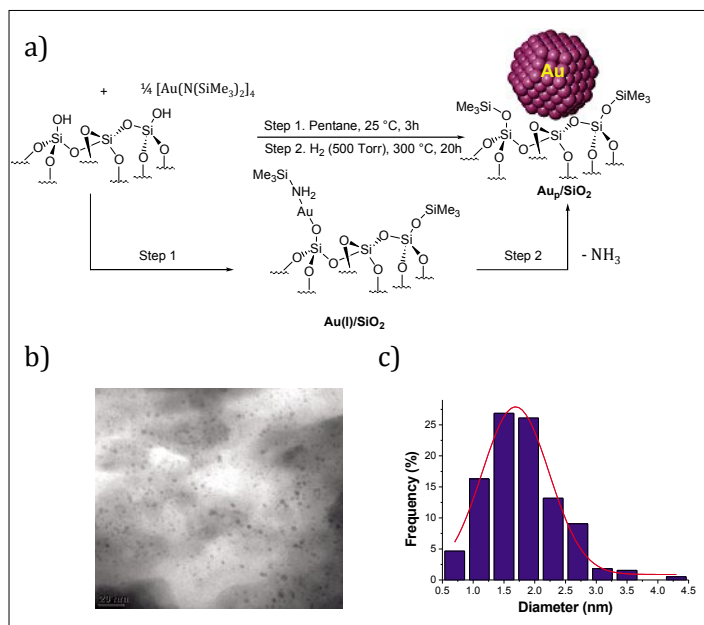


Fig. 4. a) Method of preparation of small Au nanoparticles on silica. b) TEM of Au/SiO<sub>2</sub>. c) Particle size distribution centered at 1.8 ± 0.6 nm.

### 5. Controlling the Growth of Nanoparticles on Supports: Method III

A large proportion of catalysts and devices are based on supported metal nanoparticles. For instance, they are used as catalysts in petroleum reforming technology, for the selective hydrogenation of complex molecules such as drugs, in catalytic converters, fuel cells and chemical sensors. In view of optimizing these systems both in terms of metal loading (cost) and catalytic performance (efficiency), controlling the size and the shape of the nanoparticles is thus an important target. The size is a critical parameter because it determines the proportion of surface metal atoms in particles, which are exposed to reactants. While small particles expose more surface atoms, implying a better utilization of metal resources, it also leads to a change of reactivity and selectivity. In fact, every application requires a specific optimal particle size (and shape) so that controlling particle size is key to optimize chemical processes.

Our contribution to the field has been to exploit the concept of defined site density of single-site supported ‘catalysts’, discussed above, to control the growth and the size of metal nanoparticles. This is carried out by treating well-defined supported metal complexes under mild conditions, typically upon reaction with H<sub>2</sub> at 25–400 °C, in order to remove most ligands and to grow the metal nanoparticles. For instance, with this approach, we have been able to generate small nanoparticles of Au supported on silica with a narrow size distribution (Fig. 4).<sup>[23]</sup> Here the role of the amide ligand is critical: it allows to graft 0.5 Au per nm<sup>2</sup> and to remove all silanol groups during the treatment of H<sub>2</sub>. The removal

of all OH group (passivation) is probably one of the key parameters that prevent the growth of large Au nanoparticles, which are typically obtained on silica. It is also noteworthy that these particles do not oxidize CO with molecular oxygen in the absence of H<sub>2</sub>, thus showing that that latter is involved in the activation step, probably *via* formation of surface Au–H and the subsequent formation of Au–OOH surface species.

This example clearly illustrates that controlling metal support interaction at a molecular level can provide dramatic change of reactivity and critical advantages for the understanding and designing of catalysts. We are thus exploring the ef-

fect of controlled grafting on the growth of nanoparticles and their reactivity, with the aim to develop more robust catalysts.

### 6. Research Directions and Perspectives

The aforementioned examples clearly illustrate the state of the art of our research and also delineate our future directions. We have developed a toolbox, devoted to controlling and understanding reactions on surfaces. We have had some successes, but there are plenty of challenges ahead of us, for instance in energy research and sustainable development (*e.g.* how to produce H<sub>2</sub>, how to mitigate CO<sub>2</sub>), for which catalysis will play a key role. Similarly, new breakthrough in electronic, health-care, imaging and sensing technologies will depend on the development of advanced functional materials, where controlled functionalization of surfaces is essential. While we cannot state that surface chemistry will be able to solve all these challenges, it would be impossible to think about such development without a molecular approach to surface chemistry.

Thus, our research interests will lie in understanding the surfaces of oxides and metal nanoparticles at a molecular level, and in controlling the growth of nanoparticles and eventually their shape and their interaction with the support (Fig. 5). Inspired by nature, we are also interested in finding ways to integrate molecular recognition properties as well as repair and regeneration principles in functional materials.

One of the aims is to develop single-

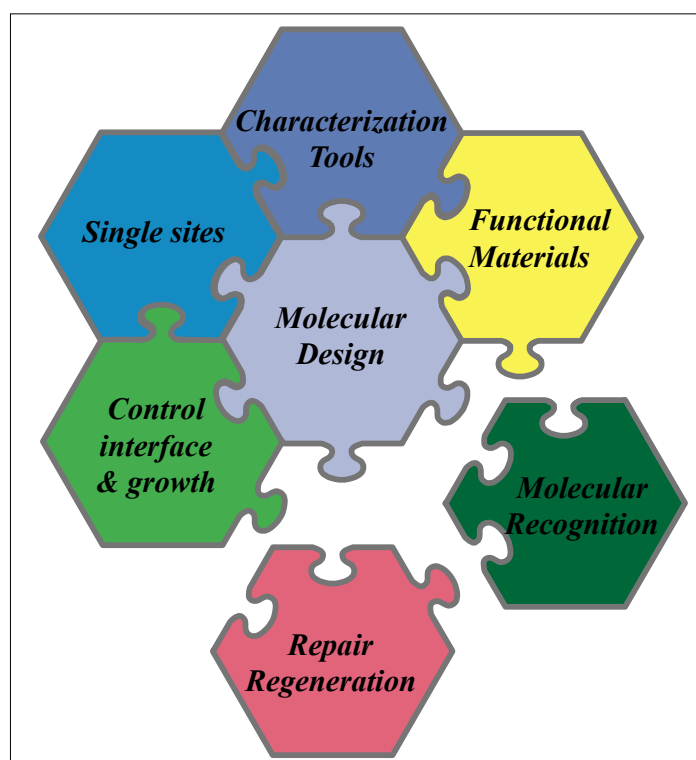


Fig. 5. Jigsaw puzzle of the design of functional materials.

site and supported nanoparticles catalysts towards the efficient transformation of petroleum and renewable feedstocks with a special focus on valorizing C<sub>1</sub> compounds. Using this approach, we are also developing luminescent nano-materials, having a molecular luminescent signature combined with the ability of molecular recognition for bio-imaging. All this requires investigating the surface chemistry of known materials but also developing new functional materials to discover improved or even novel properties. It also implies the development of more powerful spectroscopic methods in order to address questions regarding structure and dynamic of surface species in relation to their property. Our latest results in NMR show that, with Dynamic Nuclear Polarization (Surface Enhanced NMR spectroscopy) allowing signal exaltation by two orders of magnitude, new questions regarding active/surface sites can be addressed such as their structure and dynamics, their mode of interaction with adsorbates or the surface. Thus NMR spectroscopy is also a major research effort in our group, which we carry out in collaboration with the C-RMN in Lyon, our long-standing partner.

Our research group is exploring all these research areas. Please visit our website from time to time and feel free to stop by our laboratory to discover the latest developments and applications of surface chemistry.<sup>[24]</sup>

### Acknowledgments

I am very grateful to my past and present co-workers (see our webpage for a detailed list), my long-standing collaborators and to the financial support obtained over the years, whether arising from public agencies or industrial partners. I would particularly like to thank SNF, CCEM and ETH Zürich for the generous support of our research group since our arrival in Switzerland.

Received: February 28, 2012

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