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Rencontres scientifiques de l'IFP

Research Advances in Rational Design of Catalysts and Sorbents
Avancées de la recherche dans la conception rationnelle de catalyseurs et d'adsorbants

Round Table/*Table ronde*

Molecular Modeling and High-Throughput Experimentation (HTE): Meeting the Challenges of Catalysts, Chemicals and Materials Design

Modélisation moléculaire et Expérimentation à Haut Débit : relever le défi du design en catalyse, chimie et matériaux

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Panelists

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Dr. D. Farrusseng, *CNRS-IRC, Lyon - France,* Dr. S. Morin, *IFP-Lyon - France*
Pr. J.K. Nørskov, *Technical Univ. of Denmark* and Dr. C. Wolverton, *Ford Motor Company - USA*

Chairman

Hervé Toulhoat, IFP, *Scientific Direction - France*

INTRODUCTION

In what follows, it is reported the detailed account of the presentations and discussions taking place at the round table on *Molecular Modeling and High-Throughput Experimentation (HTE); meeting the challenges of catalysts, chemicals and materials design*. After the short introduction by **H. Toulhoat** *(IFP)*, each panelist gave a 5 minute contribution illustrated by slides during the first part of the round table. **S. Morin** *(IFP)*, **D. Farrusseng** *(CNRS-IRC)* and **J. Nørskov** *(Technical University of Denmark)* focused on general overviews and methodological aspects, while **G. Baron** *(Vrije Universiteit of Brussels),* **R. Chianelli** *(Texas University),* and **C. Wolverton** *(Ford)* described relevant specific examples. In the second part, questions and discussion were opened to the floor. Finally, a brief conclusion was proposed "on the fly" by **H. Toulhoat**.

Hervé Toulhoat *(IFP),* moderator of the round table, starts by recalling that the idea of this round table came from the realization that on the one hand, from the theoretical side, we are progressively gaining access to high throughput computation with the increase of supercomputer capabilities and the continuous improvements in methodologies. On the other hand, progress in computer technologies, in robotics and in mechanics in recent years allow the design of more sophisticated experimental tools, and the performance of experiments at higher rates. The particular goal of this round table is to try to assess the possible interactions between theory and experiments. Theory acts as a guide, maybe among other approaches, for high throughput experimentation. When you have new tools to experiment much faster, you have the embarrassing question of "Which experiment will be next?".

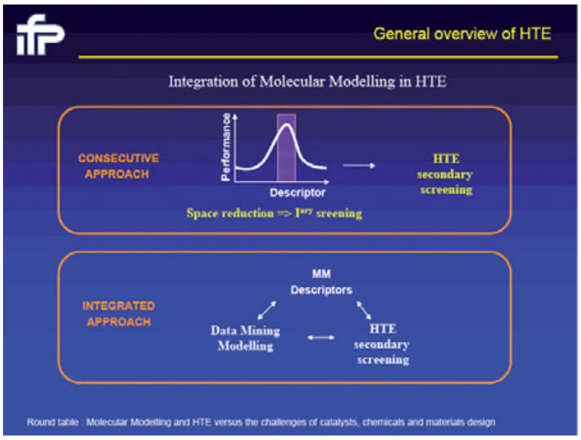
1 PANELISTS' CONTRIBUTIONS

Stéphane Morin *(IFP)* presents a general overview of high throughput experimentation and combinatorial methodologies with emphasis on specific issues for industrial catalyst development. He underlines that those methodologies appeared first in pharmaceutical and fine chemistry, and were recently developed and extended to the polymers, chemical, refining and petrochemicals domains. Concerning catalysis and methodology design, it is really a very new adventure and a lot has to be done.

These methodologies usually focus on reducing research cost and time to market, and enable the experimental study of larger parameter spaces. Concerning catalysis and materials design, the development first concerns new devices. The first few years have really been used for developing devices, which did not exist before, and which were much more miniaturized, automated and parallelized than the usual tools.

Furthermore, more recently, new research strategies were developed too. The first one, that has been applied by Symyx, is the use, following this scheme, of primary screening, which is a very high throughput primary screening, but also at very small scale. Then following this primary screening, hits are studied by secondary screening, which is done at a lower throughput (before potential industrial commercialization). According to S. Morin, the drawbacks of this approach, which is a much more combinatorial approach, at least for primary screening, are first the very low relevance and precision obtained for this primary screening, and secondly the extrapolation problem.

S. Morin describes a typical high throughput loop for secondary screening: this loop contains key steps such as the design of experiment, the preparation of sample, the screening, the data storage, and the analysis of the results (data mining, modeling...). There are some strategies to optimize mathematical tools, which are well suited when you are working with a lot of data, but also there is important work to try to integrate the maximum available knowledge. At this stage, molecular modeling has a key role to play.



General overview of HTE

Integration of Molecular Modelling in HTE

CONSECUTIVE APPROACH

HTE secondary screening

Space reduction => I^ary sreening

INTEGRATED APPROACH

MM Descriptors

Data Mining Modelling

HTE secondary screening

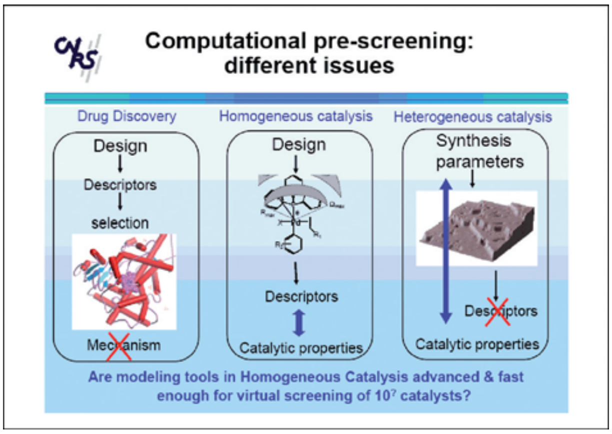
Round table : Molecular Modelling and HTE versus the challenges of catalysts, chemicals and materials design

Figure 1

Integration of molecular modeling in HTE (by S. Morin).

There are two propositions to integrate molecular modeling (*Fig. 1*). The first one concerns volcano relationships discussed during the meeting. If we could find volcanoes, or a correspondence between the catalytic performance and calculated descriptors from molecular modeling, we could use this as the primary screening, and then use HTE as the secondary screening. A more integrated approach can also be proposed by using descriptors from molecular modeling, HTE, and mathematical tools. If such a relationship cannot be found, we could try to model the relation between the first screening and those descriptors, and then by iteration, try to optimize these potential models.

David Farrusseng *(CNRS-IRC)* presents the integration of chemical descriptors in the optimization loop by raising several key questions to the audience. His first question is “Can we apply the same methodology and the same tools as in pharma (such as the primary screening or the virtual screening) to catalysis?”. In drug discovery, the space parameters are enormous and it is not possible to physically screen all drugs. Hence, they design in silico a molecule, which can be a candidate for a drug. Some descriptors are calculated which enables one to map diversity. Most of the time, it fails because the mechanism in vivo is so complex that the model is not correct (*Fig. 2*).



Computational pre-screening: different issues

Drug Discovery: Design → Descriptors → selection → Mechanism

Homogeneous catalysis: Design → Descriptors ↕ Catalytic properties

Heterogeneous catalysis: Synthesis parameters → Descriptors; Catalytic properties

Are modeling tools in Homogeneous Catalysis advanced & fast enough for virtual screening of 10^7 catalysts?

Figure 2

Computational pre-screening: different issues (by D. Farrusseng).

In homogenous catalysis, the catalyst can be precisely characterized. Because some insights about the mechanism are known, modeling the catalyst is possible and so relevant descriptors linked to the catalytic properties can be determined. From these quantitative descriptors, quantitative structure activity relationships can be extracted. In this field, the question raised by D. Farrusseng is "Are the modeling tools in homogenous catalysis advanced and fast enough for virtual screening of 10 to the power of ?" catalysts.

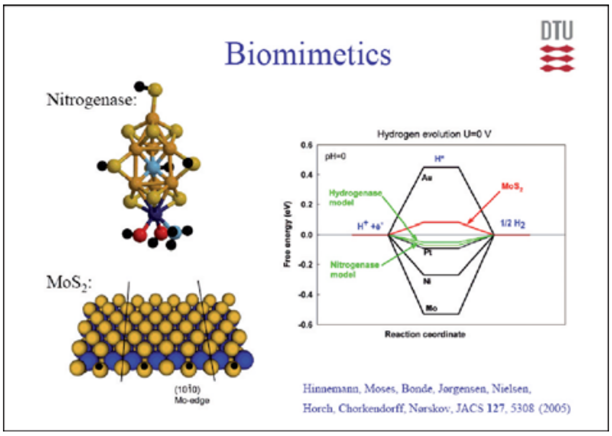
Considering heterogeneous catalysis, at least in high throughput, people do not characterize the catalyst because it is too time consuming. Instead they try to link the parameters of the synthesis directly to the catalysts and not to the descriptors of the catalyst itself implying a huge loss of information. The question is whether it is possible to fill in the lack of descriptors and go forward. D. Farusseng, recalling the example of the correlation between oxidation properties and optical basicity (a good descriptor for oxides), asks the question "Would it be possible to rediscover this empirical trend by using data mining and high throughput screening?".

Jens Nørskov *(Technical Univ. Denmark)* describes how DFT descriptors for solids and surfaces can be used in connection with catalyst design. After alerting the audience that in this field, one must understand that we are just at the beginning of being able to do anything, he puts forward three key lines that may be interesting: development of concepts, direct screening, and catalysis informatics (even if far out in the future).

The most important input that theory can give, is straight thinking about what is important and what is not important. In line with previous comments, looking for the right things in experiments is crucial. For instance, the fact that correlations (such as volcanoes) exist, is very important in defining descriptors. Actually, there is a deeper level explaining this and coming from variations in the electronic structure of the surface. Besides, there is a second factor, which is also terribly important: geometry, which may be optimized for instance by changing the interaction between the metal particles if it is a metal catalyst and the support.

Theory is very good at making links even when considering biological catalysis, where there is actually a lot of inspiration to be found. J. Nørskov reports the recent example studied in his group making the comparison between enzymes that can generate hydrogen and platinum, or even molybdenum disulfides (*Fig. 3*). So he explains that linking to other kinds of catalysis is one place where theory can also play a role because one uses the same tools.

Considering direct screening, it is actually possible to begin to look at a fair number, not 10^7, but a fairly large number of systems. Of course, these systems are currently treated in a slightly cruder fashion than what we would like to do in the future.



Biomimetics

Hinnemann, Moses, Bonde, Jørgensen, Nielsen, Horch, Chorkendorff, Nørskov, JACS **127**, 5308 (2005)

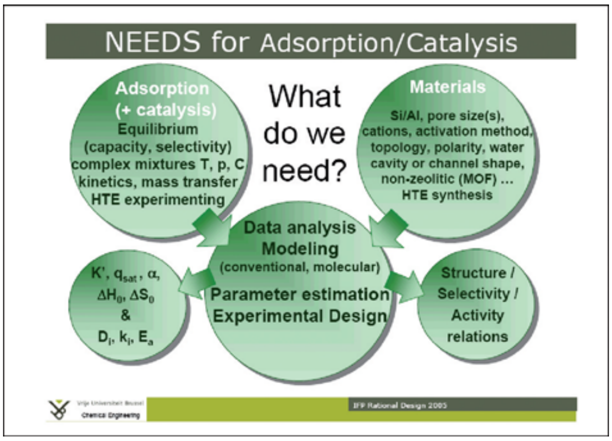
Figure 3

Biomimetics in hydrogen evolution catalysis (by J. Nørskov).

Finally, calculations are able to furnish numerous quite fundamental properties of the materials. Once a sufficient number of such properties will be available (this is certainly not done at the present time), we will have lots of data. Then in the end, data mining, or "catalysis informatics" taking experimental data and correlating it with databases to find new ways of getting to where you want to go will open up totally new possibilities.

Gino Baron *(Vrije Univ. Brussels)* presents his point of view about sorbents screening or high throughput experimentation and modeling of adsorbents, being aware that adsorption properties also have some implications on catalyst properties. He underlines that even if it is easy to invent new materials, even to prepare them, it is far more difficult to characterize them carefully and compare their properties. However, the characterization of the materials must be provided because it is ultimately needed for relations between structure, selectivity, activity of those materials, both for separation and for catalysis. As a consequence, taking the example of what is done in the VUB where parallelized and dedicated systems have been built, G. Baron thinks that it is simultaneously needed to build libraries to find all quantitative information about materials, robots and tests. Today's situation is far from the one found in the pharmaceutical industry where people can test up to 200 000 components in a short time. In the separation or catalysis fields, a massive experimental effort is needed.

As for catalysts, the question of developing adsorbents by rational design from molecular modeling can be raised. The effects are so subtle that you need more and more detailed modeling to really understand why a separation is happening and collaboration with theoreticians, being aware of the limitations of some too "ideal" level of modeling.



NEEDS for Adsorption/Catalysis

Adsorption
(+ catalysis)
Equilibrium
(capacity, selectivity)
complex mixtures T, p, C
kinetics, mass transfer
HTE experimenting

What do we need?

Materials
Si/Al, pore size(s),
cations, activation method,
topology, polarity, water
cavity or channel shape,
non-zeolitic (MOF) …
HTE synthesis

Data analysis
Modeling
(conventional, molecular)
Parameter estimation
Experimental Design

K', q_{sat}, α,
ΔH_0, ΔS_0
&
D_i, k_i, E_a

Structure /
Selectivity /
Activity
relations

Vrije Universiteit Brussel
Chemical Engineering

IFP Rational Design 2005

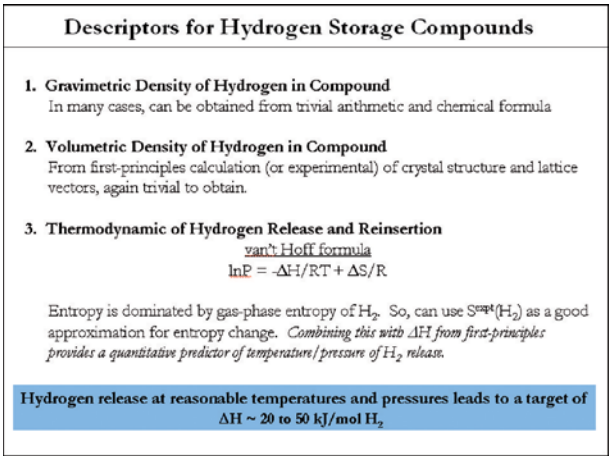
Figure 4

Needs for HTE and Modeling in Adsorption/Catalysis (by. G. Baron).

Chris Wolverton *(Ford Motor Company)* presents his experience in high throughput experimentation and modeling for the discovery of hydrogen storage materials. Ford is involved within a DOE project with UOP and a couple of academic partners in exactly this topic trying to discover new storage materials (for hydrogen storage on-board the vehicle) through high throughput means in combination with first principles modeling.

The question is again "What descriptors do you use in a problem like hydrogen storage?". The answer is slightly different from the catalysis field, maybe actually a little bit easier. One of the advantages about hydrogen storage materials is that the thermodynamics of these materials is extremely important, though kinetics is of course also relevant. Besides crucial targets like high density of hydrogen by weight, high density of hydrogen by volume (trivial to calculate if you know crystal structures), it maybe slightly more challenging to know the thermodynamics of hydrogen storage and release, governed by the ΔH of the process (*Fig. 5*). Basically from thermodynamics and simple arguments, it is possible to define a fairly narrow target for the materials needed, in terms of a ΔH of these materials. To a certain extent, a comparison can be made with the Sabatier principle, where there is an optimum to be found for the hydrogen bond strength in the material. One wants the bonding to be strong enough that one can easily insert hydrogen into the storage materials, but weak enough that it is simply and quickly extracted with minimal energy input.

The advantage of this problem is that DFT seems to be a pretty accurate predictor of this descriptor. Nevertheless, just because the storage problem has well defined descriptors, and even descriptors you can calculate, it still does not mean that we have discovered the magic hydrogen storage material.



Descriptors for Hydrogen Storage Compounds

1. **Gravimetric Density of Hydrogen in Compound**
   In many cases, can be obtained from trivial arithmetic and chemical formula
2. **Volumetric Density of Hydrogen in Compound**
   From first-principles calculation (or experimental) of crystal structure and lattice vectors, again trivial to obtain.
3. **Thermodynamic of Hydrogen Release and Reinsertion**

van't Hoff formula

$$\ln P = -\Delta H/RT + \Delta S/R$$

Entropy is dominated by gas-phase entropy of H_2. So, can use $S^{expt}(H_2)$ as a good approximation for entropy change. *Combining this with ΔH from first-principles provides a quantitative predictor of temperature/pressure of H_2 release.*

Hydrogen release at reasonable temperatures and pressures leads to a target of $\Delta H \sim 20$ to 50 kJ/mol H_2

Figure 5

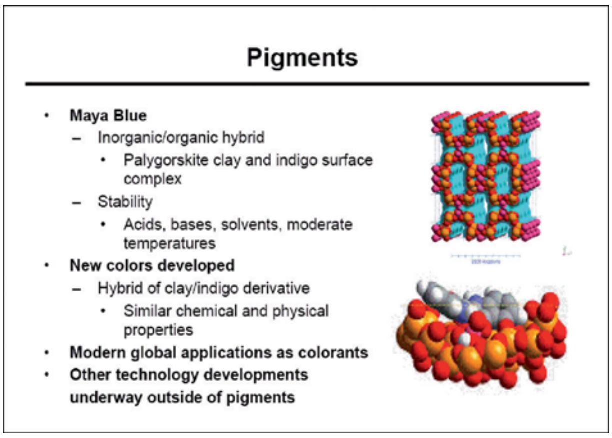
Descriptors for Hydrogen storage compounds (by C. Wolverton).

From the experimental side, there are real issues associated with high throughput synthesis of these materials: the way they are synthesized is to a large extent controlled by the high throughput ability in characterization of their sorption properties. People are investigating different means for doing that: from depositing a library of compounds spanning several domains of the compositional space, to the more brute force way of just doing lots of samples in parallel. C. Wolverton claims that high throughput characterization is an important problem in this area.

The last contribution given by **Russel Chianelli** *(University of Texas)* describes his recent successful experience in the development and improvement of pigments made of inorganic organic hybrid materials: polygorskite clay combined with the organic indigo material *(Fig. 6)*. These very cheap and easy to make materials were first found in the Maya paintings. This enterprise was so successful that a company called “Mayan Pigments” was created one year ago and has produced something like 50 or 60 new pigments.

Changing the organic molecule (indigo to thioindigo for instance) generates new colors. To understand that, they use rather simple tools of molecular modeling to determine the way the organic molecules interact with the inorganic framework (within the pore, in surface...) and to calculate the charge transfer between the atoms involved in the bonding. Furthermore, the fruitful calculation of the visible spectrum (now a validated technique) offers new ways for predicting the color.

R. Chianelli thinks that this is the future of discovery here, the fact that it is possible to calculate these properties and predicting the color. With humor, he concludes by revealing that experimentalists start getting nervous, run into their lab and start competing because they want to make the color before the theorist predicts the color.



Pigments

- **Maya Blue**
  - Inorganic/organic hybrid
    - Palygorskite clay and indigo surface complex
  - Stability
    - Acids, bases, solvents, moderate temperatures
- **New colors developed**
  - Hybrid of clay/indigo derivative
    - Similar chemical and physical properties
- **Modern global applications as colorants**
- **Other technology developments underway outside of pigments**

Figure 6

Molecular models of Mayan Pigments (by R. Chianelli).

2 DISCUSSION WITH THE FLOOR

To keep this part as lively as possible, the most relevant discussions and dialogues with the floor are reported in what follows as they took place during the round table.

Hervé Toulhoat *(IFP-moderator)*

... It is now time to open the debate to the floor. I will invite you to propose questions. It will be a round table discussion with the floor and the panelists...

Philippe Ungerer *(IFP)*

... If my understanding is correct, the development of high throughput experimentation in the pharmaceutical industry was based, among others, on combinatorial chemistry to test many hundreds of thousands of molecules. You put different mixtures of basic reactants in different proportions and you trust the almost random way of combining these reactants to produce a very large array of possible molecules... Do you think that there is an equivalent way in the industry of developing catalysts or sorbents to rapidly generate a large array of materials?

...

Gino Baron *(VUB)*

In the pharmaceutical industry, there are two different techniques. The first one you mentioned is using a library. Any of the pharmaceutical firms that have been making components over the past tens of years have 50 000 to 100 000 molecules in house. These can be tested. The techniques that are used today are that they put either a cell or an enzyme or whatever is important for a particular disease on a chip. Then they have a robotic system that goes and tips just one component after the other.

Every test takes a few seconds, so in a week, they can run 100 000 tests like that. It is a robot and you just push a button. They have these libraries. That is one approach. That is hit and run. When it hits, they look around this type of molecule and then they refine with the techniques that we all have been using.

Then the second thing is to generate molecules to be tested. That is already done in catalysis, especially homogenous catalysis, where you use combinatorial techniques to generate a whole library and then test those libraries. It has been done for a long time in the biological field with antibodies and with stuff like that. Now these techniques are not that easily transposed to heterogeneous catalysis because in most cases, you need a support, you need to put something on it, you need to activate it. These steps are very difficult to automate, but maybe we will get there one day.

The answers you get now is that you take a wafer, you put a few hundred or more catalysts on it and you just detect if it is heating up, if it is reacting or not. That is in fact very primitive in comparison to the pharmaceutical test, which can even give you numbers during such a test, so you should not look at it as if it is just something simple. It is a complicated test and you can do a lot of analysis from it. That is one of the points I said.

We still have a long way to go to develop the technology even for the experiments there. I personally do not readily see how we can do that. It is going to need more work.

Hervé Toulhoat *(IFP-moderator)*

As far as I know, they are also heavily using the QSAR approach, trying to introduce a lot of descriptors.

Russel Chianelli *(Texas Univ.)*

I just have a question for the panel. If you read *Science*, *Nature* and popular science press, it seems as if the results are mixed. I would like to ask the panel if that is true?

Gino Baron *(VUB)*

As far as I know from the field, there are hits that were found because people have components and all of a sudden, a drug which was designed really gradually by adding pieces to the molecule to optimize for a particular disease, all of a sudden seems active for something else. Sometimes they know the region where they have to search. They do not have to search blindly because they know that there is, for instance, a side effect with it. Viagra is one of the examples, where it was originally developed for something totally different. This is maybe the best example. You often see it by side effects.

David Stern *(Exxon Mobil)*

The drug discovery example is pretty interesting. It brings up a couple of points. One that it brings up is the role, and we were just discussing it earlier, about establishing a primary screening and going through testing. The second part of this involves a question of serendipity and how we advance catalysis based on serendipitous discoveries that we are not really looking for, that you had brought up earlier.

I wonder what the panel thinks of what the future of high throughput experimentation is going to be? Is it going to be a lot more Edisonian in its approach, where we are looking to refine a particular catalyst system, where we could do orders of magnitude more experiments, or do we think it is going to be used more as a research tool to look for new types of paradigms in catalysis?

David Farusseng *(CNRS-IRC)*

Of course, there are many issues and I would say that high throughput experimentation is not a strategy, it is a tool. You can use this tool in various ways. I would say one way maybe is to give us a chance to discover new materials. For example, every year, A. Corma in Valencia discovers new zeolites. We may not know the application, but you can foresee applications for sure. Also I would say you can push the limit and discover new reaction pathways, for example.

It was said many times in conferences about high throughput. So for sure, high throughput experimentation can give new breakthroughs, but you cannot predict it. You do not know how you will have this hit. For sure, I think you have to suffer before having a good hit. This is my opinion. Even if you can screen 1000 or 10 000 catalysts a day, I think you have to suffer anyway.

Russel Chianelli *(Texas Univ.)*

Well, I would say, to me it is obvious that when you get the theorists and experimentalists working together in the right atmosphere, you are going to get good results. They just feed on each other. You mentioned the word "serendipity". When I was at Exxon, if I used the word serendipity, I went down 10 points in the rating because serendipity was luck and therefore bad management. You could not plan for it. I just add to it: if you have the right mix of theory and experiment, then you allow "serendipity" to operate.

Hervé Toulhoat *(IFP-moderator)*

You also have targets.

Gino Baron *(VUB)*

You will never bluntly start searching for catalysts. You have to specify what for, so that will automatically limit us strongly already because of the knowledge we have. The same holds for sorbents. I can tell you by looking at a range of components or a range of materials, we have discovered two new mechanisms for separation, which we would not have found without those techniques because we would never have done as many experiments. That might be something that helps. "Serendipity" kicks in and you are aware when you are doing that, so you still have to plan so much that you look at your results.

The biggest problem according to me is "How are we going to deal with those results?". Maybe even further, libraries and companies are full of results that already exist over all those years. I think they are worth mining, provided we know enough about the conditions in which they are done, and that is a very big difficulty, as you might know.

...

Pascal Raybaud *(IFP)*

Concerning the concepts that can be extracted from HTE data combined with molecular modeling, "will HTE facilitate the finding of new concepts, helping us to make a breakthrough ?". Having a close look at the volcano curve concept, applied to sulfides or even to ammonia synthesis for instance , we see a well defined maximum on volcano curves, and apparently we will never find a catalyst providing a significant breakthrough as people would expect to have because commercial catalysts are already very close to this maximum. In this area, is it not also a matter of now designing a new formulation with other constraints such as lower costs, or environmental?

David Farusseng *(CNRS-IRC)*

Let us remember the superconductor story. In the 90s, theoretical models predicted a maximal temperature for superconduction. Then one experimentalist has discovered a new material which overcome this maximum temperature. We have to keep in mind that a model is based on a given mechanism. There might exist other reaction pathways which can be only identified when new types of materials are prepared and tested. Then, alternative models can be built on the basis of new knowledge and assumptions. HTE is a very appropriate tool to discover new materials by screening while having very different thinking. I think we should not limit our mind by models, but if we want to have breakthroughs, we have to think differently.

Hervé Toulhoat *(IFP-moderator)*

Can we state at this point that usually when we are dealing with catalysis, we have one reaction in mind? We have a target. We are trying to make products in better conditions. It already implies that we have some idea of what kind of chemistry will help us to achieve this target in terms of conversion and selectivity for this reaction. If not, maybe high throughput experimentation can help us by systematic screening, also, of operating conditions to define, for instance, the range of temperature and partial pressures which is adequate for this particular target. Then maybe it will help to build a new kinetic model.

Jens Nørskov *(DTU)*

There is the question about having a volcano saying "This is the best you can do". This of course is extremely dangerous, as was also pointed out. The reason is that one volcano comes from one set of correlations and when you could move to a new class of materials, those correlations change. I think this is a good example where concepts are important, so if you know what is behind the volcano, then you also know when you can use them and when you cannot use them. Let me just give an example: I was showing two different Brønsted-Evans-Polanyi relationships, one for steps, one for flat surfaces. It actually means that you have a volcano with different maximums for two different surface geometries. If you can make a system with a new geometry, you have a new BEP relation and you actually have a new maximum. Yes, one should never just take one volcano and say, "This is it". On the other hand, we actually do begin, at least for simple systems, to have the insight to know when to use it and when not to use it, perhaps even to look to new systems. I think yes, be careful, but do not be discouraged.

Hervé Toulhoat *(IFP-moderator)*

I totally agree with you. One volcano may hide another or you may also end up with several.

Jens Nørskov *(DTU)*

You demonstrate by what you can make. If you can find new ways of making similar things and move to new classes of systems, I think that is actually perhaps the most exciting part. So if you move away from metals, which is what we are all doing, there is an enormous phase space of uncharacterized, at least, systems when you move to oxides, sulfides. I'm thinking of carbides, nitrides, lots of other ways, so I think one should certainly never say, "It can never get better".

On the other hand, there is another thing that gets back to a point that was raised earlier. If I understood your comment correctly, I agree that probably the most important thing is content, and what is important, what is not important. When it comes to how you screen, then of course one should just do it in the simplest possible way.

The real question is how do we do it most efficiently and cheapest? Whether that is experimentally or by using computers, I think that it is up in the air. I think at the moment, probably for most systems, it is much cheaper to do it experimentally. My guess is that if you look at the price of doing experiments and compare it to the price of doing calculations, we know that the price of doing calculations drops exponentially. That is perhaps not the case with the price of doing experiments?

I think there is a good chance that for systems where we actually know what we are after, then that one day, it will become much cheaper to do it experimentally. I think that is the only reason to do it. From a conceptual or intellectual point of view, I think the most important thing is to actually know what you are doing and I think that helps no matter how you then screen.

Russell Chianelli *(Texas Univ.)*

I would like to add to that statement because I get a little nervous when I hear costs. We are scientists and engineers and theoreticians and so on. The best thing about the theory in my estimation is that the thinking gets better in a group. Somebody said that. I think that is the real benefit. In 20 years from now, would you like that we would not have a conference like this because there would be a bunch of machines putting everything out and they do not need us anymore?

Claude Henry *(CNRS)*

Some people say that when we do a combinatorial or high throughput screening, we have no time to characterize our sample. I think it is a very, very bad problem because for example, take the cases of catalysis by gold. If we do simply it by a classical impregnation method, we have relatively big particles and we will never see the catalytic properties of gold because it is only when we size it down to 3 nm that these properties appear. I think that the catalytic properties are not only a mixture of elements, but we have to take into account the structure of the material, the size of the particles, the morphology and you have seen a lot of examples where the morphology is very important.

Gino Baron *(VUB)*

I absolutely agree. It does not make sense to screen materials or even test them more thoroughly if you do not know what you are dealing with because you will one day have to make the sample again and know what is the link, of course. Also, high throughput techniques exist for characterization. You have X-Ray Diffraction equipment today, many other techniques like spectroscopic techniques, which are automated, DGAs and whatever. One of the techniques we have been using over the past year is just to use probe molecules and measure adsorption, like you do a nitrogen isotherm to measure porosity or pore size distribution. You can use other molecules and probe for some properties. That can be done very quickly. Even one case, where we could do it together with a synthesis, where a material was synthesized, then treated and on the same robot, we did the characterization. A very primitive one, I agree, but I think this could be developed for the future. You are absolutely right, there is work to be done there.

...

Hervé Toulhoat *(IFP-moderator)*

In a sense, the background we have on the characterization has the same role as molecular modeling or theory because it is an input of knowledge, which is, of course, always needed.

David Farusseng *(CNRS-IRC)*

Maybe what I can add, at least in the big companies like Exxon or others I guess they do characterize good catalysts, but not the catalyst that has zero activity. For academics, we try to use another approach: we actually try to characterize all the components as much as possible in order to find relationships between particle size or adsorption capacity or whatever, with the catalytic properties. But these are two different targets one is to discover more knowledge and the other is more for screening and discovering materials. Maybe big companies are doing that also, but you see they are two different strategies. Again, HTE is a tool and you can use it differently for different targets.

Michel Daage *(Exxon Mobil)*

I want to return to this because I think that it is not an issue of being in academia or being in industry. I think we are dealing with the same kind of problems. We need to know where we are going and depending on how we are going to do it, we will be using different strategies combining HTE with modeling. I think it is important not to look at it as "ExxonMobil is not going to do the fundamentals because they are only interested in an industrial catalyst". The fundamentals are important to us and what we do: it is in the fundamental understanding that robust solutions to practical problems are found. We are scientists and that is the reason we are here.

It is true that at the same time, industry needs to worry about scale-up because we use catalyst in ton quantities and in very large reactors. If you try to look at these challenges and their potential solutions, HTE equipment will be used in different ways at different phases of the work. I am surprised to see that the panel has a tendency to go toward "There is one way of doing this" and I think that it is not the case: I believe that there are multiple options; some of them allowing to look at and resolve problems with a high dimensionality. The opportunity to resolve high dimension problems is where answers are going to be. It will include a high level of integration between the "robot", the modeling, data mining and experimental design.

Hervé Toulhoat *(IFP-moderator)*

We have prepared a question here, and maybe you have the answer right now: "How can we prevent the approach which combines molecular modeling and HTE from muzzling the key role of intuition?". I think it should be a way to liberate intuition, but on a more scientific basis.

Russell Chianelli *(Texas Univ.)*

We have to create the right environment for the intuition to operate. That means people working together, theorists and so on, and I might just say something a little bit controversial. I think that the rapid throughput using computers has a bright future, but using libraries of heterogeneous catalysts, I do not think so.

Gino Baron *(VUB)*

From my point of view, I can only say that I completely agree with that and the place of intuition should remain entire.

Jens Nørskov *(DTU)*

The small comment I wanted to make is that intuition, to me at least, is using the right concepts and I think you best develop these in a combination of calculations and experiments. I think a lot of the concept development actually comes from being able to look at not just one system, but a whole host of different systems, looking at trends. We are really marrying the looking at a large number of systems and developing concepts that you need.

Hervé Toulhoat *(IFP-moderator)*

Intuition cannot stay as intuition. It has to evolve into concepts.

Pascal Raybaud *(IFP)*

My specific question is now for Chris Wolverton. In the field of hydrogen storage research, in your close environment, do you have some experience in HTE for searching for new materials? How is it undertaken at the moment in combination with what you presented on the molecular modeling investigations?

Chris Wolverton *(Ford)*

To be fair to the field in this particular area (HTE applied to hydrogen storage materials discovery), it is very new. At least the groups that I know of who are doing this, have been doing this on the order of a year, not a decade. In many cases, it is probably currently more accurate to say medium throughput. In any case, because of that, at present the sort of configurational phase space that people are looking at is relatively limited and hence, I think that this issue that we talked about before is critical: in our field at the moment, it is probably more important to have the creativity and the intuition and the understanding to design the experiments you are going to do to serve as essentially the initial screen, than the gain you are getting from the high throughput at this point. Over time, though, hopefully the throughput of HTE in this field will increase and then, not that intuition goes away, the benefits of HTE will become larger and larger.

Regarding the experimentation, I would say that we are faced with some of the same difficulties that I hear from the catalyst folks, that there are groups that are depositing libraries of samples. In some cases, the libraries of samples are not physically separated from one another. They are just sputtered onto a target, exposed to hydrogen and then, since the hydriding reaction is often exothermic, you just look for hotspots on the library.

Other groups are taking a different approach and are using robots to automate the synthesis of many physically different samples and actually putting them into more precise sorption apparatuses and really test absorption or desorption one by one, but just in parallel. I am slightly biased because I am involved in one of those types of experimentation and not the other, but I think both have promise and we will have to see which approach proves more successful.

Wilfried Mortier *(Exxon Mobil)*

I think that you have to make the fundamental difference between discovery which is all or nothing and the data that we need, and as a secondary screening, where that has to go along with good characterization, good data. You need absorption data, you need catalytic data, you need material characterization as secondary screening... Primary screening is something different.

Gino Baron *(VUB)*

Personally, I am doing secondary screening and I am not at all involved in doing the primary because I do not see how this could help us. We already know quite a bit when we start a problem and so we know where to look. Unless you get the details right, it does not help because one day, you will have to scale up and to even think about scaling up, you need very good data to start with and good characterized materials. It has been said over and over again here.

I think the secondary screening is something that still needs a lot of development. It is much more complicated, but in combination with theory, with our modeling, it is probably the thing that is going to help us the most in the coming years. It just speeds up what industry has been doing for a long time. Go to most of the industries they have rows of pilot plants testing catalysts, which already are fairly refined and just trying to get the conditions right. Now this can be done much faster, so I think that is one of the advantages of those systems.

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CONCLUSION

This part aims at briefly sorting some highlights out of the presentations and debate, according to the reporters' perception. Indeed the exchanges were rich, eventually controversial. We felt it might be helpful for the readers to distinguish between statements where consensus was reached, and open questions:

Statements of general consensus

- High Throughput Experimentation (HTE) aiming at accelerating innovation in terms of catalysts and sorbents is so promising that most or all leading players in academia or industry are currently engaged in this methodology.
- Most projects involve directly "secondary screening" because it is felt that a precise information on reaction rates and selectivities is needed to readily up-scalable and well characterized materials.
- Most people are "learning on the fly" since the field is still new and very difficult technically.
- What has to be learnt is not only how to prepare catalysts, characterize, and test catalysts reproducibly at (moderately) high throughput, but also how to manage and exploit the flux of information, and how to monitor the "loops" in order to converge to targets.
- Chemical and physicochemical concepts are expected to provide guidance as well as to emerge from HTE. Data mining and statistical analysis methods, evolutionary algorithms, and other mathematical angles of attacks are necessary but not sufficient.
- Molecular modeling is indispensable in helping the process both for adsorption and catalysis, providing descriptors but also a way of thinking: working concepts ultimately emerge from thinking, which elaborates over intuitions.
- Molecular modeling tends towards High Throughput Information generation as well as HTE. The task we are facing is thinking from a lot more systematic and consistent data.
- HTE implies that theoreticians, characterization people, catalysis people, chemical engineers have to work closely within trans-disciplinary teams, to talk to each other.

Open/controversial questions

- Libraries of catalysts will be useless or useful.
- Screening is for all or nothing as opposed to exploring systematically the parameters space.
- There are many ways to combine molecular modeling and HTE and nobody to date is in position to show the best if any.

The specificity of this Round table amid numerous similar discussions on HTE for catalysis in the past few years has certainly been this emphasis given to what can be expected from the *combination* of modeling and HTE. Through the next 3 or 4 years a high throughput of data and expertise with flow: it is a very enthusiastic perspective for participants to READICATS and other colleagues in the field. Therefore “Rendez-vous” on this time scale with proved concepts and flaring results for READICATS II.

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