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Dossier

Discovery and Optimization of Catalysis and Solvents for Absorption Using High Throughput Experimentation
Découverte et optimisation de catalyseurs et d'absorbants par expérimentation haut débit

Knowledge Based Catalyst Design by High Throughput Screening of Model Reactions and Statistical Modelling

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Résumé — Conception de catalyseur par criblage à haut débit de réactions modèles et modélisation statistique — La définition et la préparation de matériaux sont des étapes clés dans le développement de catalyseurs. Celles-ci peuvent être effectuées de façon empirique et/ou à partir de bases théoriques. Par ailleurs, l'expérimentation à haut débit, technologie récente, permet d'accélérer l'optimisation de formulations catalytiques par exemple par criblage systématique d'un espace d'étude prédéfini. Cet article a pour objet de développer une méthode QSAR (*Quantitative Structure Activity Relationship*) basée sur la recherche de descripteurs cinétiques et mécanistiques, dans le domaine de la catalyse acide et métallique supportée. Des caractéristiques physico-chimiques (descripteurs) d'une soixantaine de catalyseurs bimétalliques ont été mesurées suivant leur performance dans deux réactions modèles : l'hydrogénation de l'*o*-xylène pour rendre compte de la catalyse par le métal et l'isomérisation du diméthyl-3,3-butène-1 pour la catalyse par les sites acides. Ces descripteurs ont été ensuite mis à profit pour modéliser les performances d'une vingtaine de catalyseurs dans une réaction complexe : la déshydrogénation du *n*-décane.

Abstract* — *Knowledge Based Catalyst Design by High Throughput Screening of Model Reactions and Statistical Modelling — *Material design and synthesis are key steps in the development of catalysts. They are usually based on an empiric and/or theoretical approach. The recently developed high-throughput experimentation can accelerate optimisation of new catalytic formulations by systematic screening in a predefined study domain. This work aims at developing a QSAR (Quantitative Structure Activity Relationship) method based on kinetic and mechanistic descriptors for metal and acid catalysis. Physico-chemical features of approximately sixty bimetallic catalysts have been measured according to their performance in two model reactions: xylene hydrogenation for catalysis on metallic sites and isomerisation of 3,3-dimethyl-1-butene for catalysis on acid sites. These descriptors were finally used to model the performances of around twenty catalysts for a more complex reaction: n-decane dehydrogenation.*

INTRODUCTION

High Throughput Technologies (HTT) has revolutionized the research and development of new drugs in the pharmaceutical industry. Today, the same paradigm change is taking place progressively in the bulk and specialty chemical industry [1-5]. As such, HTT enable to accelerate the development of new materials and processes and represent a concrete answer to world concerns for efficient use of sustainable energy and resources, safe chemical products and environmental protection.

Today, HT experimentation has matured and is almost regarded as commonplace. We can assume that more and more of the solid catalysts put on the market have been developed by means of HTT, at least partially, at a given step of their development. The combined optimization of material formulations enables to reduce the time to market. However, breakthrough discovery cannot only rely on the systematic screening of libraries of ever increasing size. The basic HT approach is not appropriate to discover novel knowledge. In addition, the brutal HT screening approach does not take advantage of the previous knowledge generated in previous screening projects.

There is thus a strong motivation to shift from a "statistical design" approach to a "rational design" for the development of solid catalysts [1]. This knowledge oriented approach aims at predicting *a priori* catalysts features and performances based on physico-chemical descriptors. In other words, the development of catalyst profiling methods shall enable the pre-screening of candidates by simulating of performances of virtual catalysts. In the domain of drug discovery, this general approach is known as "Quantitative Structure-Activity Relationship" (QSAR). It aims at linking "descriptors" of the molecule structure with "performances" of the molecule. The descriptors are supposed to capture the physicochemical features which are relevant to performances modelling and predictions.

Following this general QSAR concept, two different routes that include the calculation and/or measures of descriptors have been investigated for the development of solid catalysts. Klanner *et al.* [6, 7] have calculated a series of physico-chemical indices of a large library of solids including complex oxides and metal supported catalysts based on the catalyst formulations and physical constants. These indices have been designed to potentially characterize bulk and surface features. Then, data mining techniques were used to select a set of most discriminant indices which are finally used as descriptors for the catalytic performances [8]. The main limitation of this method is the large number of possible indices which makes their selection difficult. Furthermore, experimental information can also be added to the series of indices. Researchers at ITQ (Instituto de Tecnologia Quimica) have applied this solution through the use of readily-available HT characterization techniques in order to acquire multivariate spectral descriptors (catalyst fingerprints) useful for QSAR modelling [9]. This approach was validated for the HT screening of 320 mesoporous titanium silicate materials for the epoxidation of cyclohexene [10]. In order to assess long-distance features, all catalysts were analysed by X-ray Diffraction (XRD) and further classified into distinct families according to XRD pattern similarities (using PCA (Principal Component Analysis) and clustering techniques). The authors demonstrated that the use of this information enabled a significant improvement in prediction rates.

QSAR and virtual screening methods based on descriptors continue to represent a challenging objective for heterogeneous catalysis, with no method yet guaranteeing diverse properties of solids in the context of library design. It is the high complexity of solids, compared to molecules or drugs, which makes the design of libraries a serious challenge. One of the main hurdles is therefore the description of a solid, especially if the solid has not been synthesized in reality and presents no available characterization results. High throughput characterisation tools are still in early stages and the access to reliably measured properties of materials is far more limited compared to the synthesis and testing data generated by HT techniques.

In this study, we show an alternative QSAR approach for the development of solid catalysts which overcomes

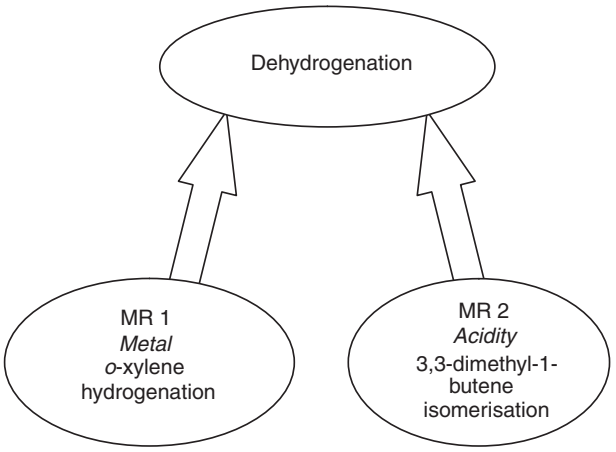


Figure 1

Modelling a complex reaction from model reactions (MR).

the issues of physical characterization of solids. The main assumption is that relevant catalyst descriptors can be experimentally captured by measuring activity and/or selectivity from a series of model catalytic reactions. We describe a QSAR approach which can predict catalytic performances of catalysts for the dehydrogenation of long chain paraffins from two distinct model reactions (*Fig. 1*).

Two main advantages of using model reactions to quantify catalytic properties can be cited:

– mechanisms are usually well-known or at least well-documented, so that catalytic results can be interpreted according to physicochemical principles. For example, the conversion of isopropanol is a classic mean of characterizing the surface reactivity of oxides. The reaction products leave a fingerprint: propene formation indicates Brønsted acidity, while isopropylether is the sign of Lewis acidity, and acetone reveals that the surface can be reduced [11];
– the use of simple reaction mixtures and the absence of industrial constraints make it easy to set up the appropriate reactions. Model reactions are simple and easy to run: reactants and products are few and can be analysed quickly. This allows a high turnover of runs. Side products are inexistent or limited within the operating conditions. Finally model reactions have simple kinetics. They are operated under kinetic control: their initial activity rate is easy to estimate accurately, it is specific to the material tested and it provides a good summary of the physicochemical properties of the material under operating conditions close from industrial ones.

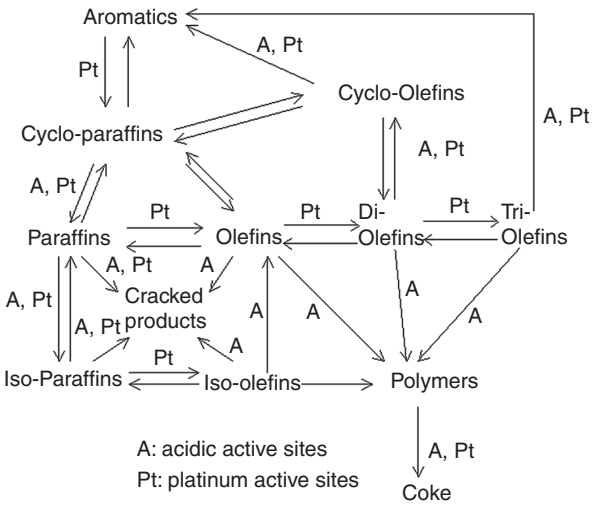


Figure 2

Various mechanisms related to the reaction of dehydrogenation of long paraffins.

1 METHODS

1.1 Target Reaction: *n*-Decane Dehydrogenation

Dehydrogenation of long chain paraffins (nC_{10}-nC_{14}) plays a key role in the formation of linear alkylbenzenes, essential for the production of detergent. Dehydrogenation of *n*-decane is a valuable representative of this family of reactions. It is a very endothermic reaction and conversion is strongly limited by thermodynamics. Operating conditions are kept to low pressure (1 to 5 bar) with hydrogen to limit deactivation. Conversion is usually low, 10-15%, which heavily limits the production of olefins. There is no use to operate at higher temperature than 773 K because any improvement of the overall conversion is counter-balanced by the shift of selectivity towards unwanted side reactions such as cracking, isomerization and aromatisation.

Common catalysts for this reaction are Pt-Sn supported on alumina. Hydrocarbon activation and dehydrogenation take place on platinum particles. The latter have been known to show the strongest capacity of hydro/dehydrogenation, since Tetenyi *et al.* [12]. Tin or similar promoters improve the stability of the catalyst as well as its selectivity towards long chain linear olefins. Finally material acidity is carefully controlled thanks to the addition of alkaline/alkaline-earth metals. The purpose of this is to limit as much as possible acid or bifunctional reactions leading to aromatics, isoparaffines or shorter hydrocarbons from acidity-based cracking.

Figure 2 illustrates the complexity of the various reactions connected to dehydrogenation of long chain paraffins.

1.2 Model Reactions

1.2.1 Choice of Reactions

The choice of the model reactions is conditioned by the chemistry involved in the reaction of interest. Hence, information obtained from testing the catalyst in model reactions shall capture all relevant properties involved in the dehydrogenation of long chain paraffins (nC_{10}-nC_{14}). It involves the following catalytic reactions:

1. dehydrogenation of paraffins in olefins on metallic sites; these reactions are at thermodynamic equilibrium with dehydrogenation of olefins in diolefins and triolefins (not desorbing);

2. isomerisation of paraffins in iso-paraffins; it is usually attributed to acid sites (*via* the relevant olefins and iso-olefins) of weak to medium strength but it is possible that a metallic mechanism is at stake;
3. formation of aromatics by cycle closure (essentially mono- or di-*ortho*-alkylaromatics); several metallic or bifunctional mechanisms are involved;
4. cracking on acid sites (after isomerisation) or metallic sites (hydrogenolysis);
5. coking.

In this study, we assume that the metallic properties of the catalysts involved in the reaction of *n*-decane dehydrogenation can be probed by measuring the catalytic performances in hydrogenation of "aromatics", while the acidity properties can be quantified by measuring the performances of double bond shifts isomerisation.

Among hydrogenation/dehydrogenation reactions, we chose the *o*-xylene hydrogenation. Hydrogenation and dehydrogenation reactions are equivalent in terms of characterisation of the catalytic activity due to metallic sites. This allows the descriptors derived from the model reaction to be used against other complex reactions involving metallic catalysis.

Hydrogenation of *o*-xylene is a well-documented reaction, simple enough since it has only two products: *cis*- and *trans*- dimethylcyclohexane. It was also reported that the *cis:trans* selectivity may characterise the electronic density (Fermi level) of the metal particles [13-15].

Model reaction involving double bond shift is well suited for the characterisation of Brønsted acidity. Indeed, this class of reaction offers the possibility of selecting a probe molecule for given level of acidity. For example, the isomerisation of 1-hexene is particularly well suited for characterizing strong sites whereas 3,3-dimethyl-1-butene (33DMB) can be used to quantify the acidity of weak acid sites as found in alumina supports [16-18].

1.2.2 Experimental Workflow

Table 1 shows the workflow for the different model reactions, described in the following paragraphs, to the exception of deactivation handling, which was detailed in previous articles [17, 22].

The kinetic model of hydrogenation of *o*-xylene is more complex, showing a higher number of parameters. Ranking the catalysts by hydrogenation activity (under the same operating conditions) was possible but the wealth of diversity encapsulated in the set of kinetic descriptors would have been lost in the process: an object is better described by two non-correlated descriptors than by one. This is why data mining and mapping tools were used to preserve as much as possible this diversity.

TABLE 1
Data workflow for reaction model study

o-xylene hydrogenation	33DMB isomerisation
Raw data acquisition	
Validation of raw data	
Validation of a deactivation model [22]	
Retrofitting of testing data to get purely kinetic results, discarding deactivation [22]	(Deactivation had limited impact) [17]
Validation of a kinetic model	
Acquisition of kinetic parameters	Retrofitting of testing data to simulate iso-condition activity
Data mining and mapping of kinetic descriptors	Ranking of samples

1.3 Catalyst Descriptors Deriving from Model Reaction Testing

Traditionally, the relative comparison of catalysts is performed using measurements such as conversion at a given condition or selectivity at given conversion levels but the disadvantage of defining a figure of merit at a single conversion or temperature is that this disregards some of the data collected. Indeed, for a given condition some of the conversion data from a very diverse library of catalyst would be either null or 100%. As an alternate strategy, the apparent activation energy and prefactor of each catalyst can be calculated from a kinetic model, allowing much finer comparison. The activation energy and prefactor can be used as performance descriptors themselves over a certain range of temperature or can be used to calculate various figures of merit as needed, such as the conversion or reaction rate at any arbitrary temperature or the maximum conversion and its corresponding temperature. This method was applied by Ford Research Laboratory with the aim of assessing synthesis parameters for Pt-based NO oxidation catalysts [19]. Hence, the use of empirical models enables the proper ranking of catalyst activity. However, values of apparent activation energy or pre-exponential factors are quite disconnected from solid bulk or surface properties. On the other hand, kinetic modelling can better describe the intrinsic features of the catalysts [20]. Heat of adsorptions of the substrates and products, activation energy and reaction orders which are characteristics of the catalysts are typical parameters of a kinetic models.

Kinetic parameters are useful to describe a catalyst but also to quantitatively compare all catalysts for which the same kinetic model is fitting. The wider the diversity of the catalysts e.g. with different metallic sites, dopants or supports, of which activity follows the same kinetic equations, the more useful it is to compare them. Hence, kinetic parameters are very appropriate to be used as potential descriptors for a complex reaction as long as the complex reaction shares common mechanistic features.

For the *o*-xylene hydrogenation (MR1), the rates of formation of products *cis*- and *trans*-dimethylcyclohexane (DMCH) have been modelled by the following equation:

$$r_i = k_i \frac{K_{oX} p_{oX} \left(K_{H_2} p_{H_2}\right)^{n_i}}{\left(1 + K_{oX} p_{oX} + \sqrt{K_{H_2} p_{H_2}}\right)^2}$$

where i stands for *cis*- or *trans*-DMCH ($i = 1$ and 2 for *cis*- and *trans*-DMCH, respectively), k_i is the rate constant, which follows the Arrhenius law:

$$k_i = A_i e^{-\frac{E_i}{RT}}$$

K_{oX} is the equilibrium constant of adsorption of *o*-xylene:

$$K_{oX} = e^{-\frac{\Delta H_{oX} - T\Delta S_{oX}}{RT}}$$

K_{H_2} is the equilibrium constant of adsorption of hydrogen (same notation as K_{oX}) and n_i is the hydrogen partial reaction order. Parameters p_{oX} and p_{H_2} are the partial pressures of *o*-xylene and hydrogen, respectively.

Therefore, the catalytic activity of *o*-xylene is described by nine parameters:

- pre-exponential factors A_{cis} and A_{trans},
- activation energies E_{cis} and E_{trans} in kJ/mol,
- entropy of adsorption of *o*-xylene in kJ/mol/K (noted S_{oX} from now on),
- enthalpy (kJ/mol) and entropy (kJ/mol/K) of adsorption of hydrogen (noted H_{H_2} and S_{H_2}),
- partial pressure orders n_{cis} and n_{trans}.

Selectivity is described by a different set of parameters, derived from the ones above:

- ratio A_{cis} / A_{trans},
- difference $E_{cis} - E_{Trans}$ in kJ/mol,
- enthalpy in kJ/mol and entropy in kJ/mol/K of adsorption of hydrogen (noted H_{H_2} and S_{H_2})
- difference $n_{cis} - n_{trans}$.

In the case of isomerisation of 3,3-dimethyl-1-butene (MR2), the catalyst activity is directly correlated to the acidity of the material hence the kinetic model was used to calculate the catalytic activity – later used as the descriptor for this reaction – at the same temperature and partial pressures for all the samples.

A simple kinetic model ($r = k.C^n_{33DMB}$) was built to describe the isomerisation reaction. Preliminary tries on unmodified supports have shown that conversion was constant when partial pressure of reactant was taken between 0.02 and 0.1 bar and temperature around 533 K. This indicates that the order of 33DMB partial pressure is equal to 1.

Therefore reaction rate (mol·m^{-3}·h^{-1}) is:

$$r_{iso} = p^0_{33DMB} \frac{(X-1)\ln(1-X)}{m_{cata}} q_{tot}$$

with p^0_{33DMB}, reactant initial partial pressure (bar); X, conversion; q_{tot}, total molar flow (mol·h^{-1}); m_{cata} (g), catalyst mass.

The descriptor of acidity (r_{iso}) is calculated as the reaction rate at the same 33DMB initial partial pressure (0.06 bar).

The QSAR can be written as the mathematical expression that links the descriptors obtained from the model reactions to the performances of the complex reaction. In this study, the mathematical expression is a multilinear function of the first order:

$$(y_1, y_2, \cdots, y_n) = \text{function}\ (A_{ci}, A_{trans}, E_{cis}, E_{tran}, S_{oX}, H_{H_2}, S_{H_2}, n_{cis}, n_{trans}, A_{cis}/A_{trans}, E_{Cis} - E_{Trans}, n_{cis} - n_{trans}, r_{iso})$$

where y_1, y_2, ..., y_n are performance indicators based of activity/selectivity data of *n*-decane dehydrogenation as described in Section 3.3.

2 EXPERIMENTAL

2.1 Catalyst Library

A combinatorial library of more than 60 supported bimetallic samples was prepared. Catalysts were made by combining a main hydrogenating metal among Rh, Pt, Pd and Ni, a secondary element as additive among five possibilities (Mo, Mn, Sn, Ag, In) and two distinct alumina supports (high and low surface area, respectively δ- and θ-alumina, respectively designed by the letter A and B in the catalyst name). The catalysts were prepared by incipient wetness impregnation starting from chlorine free precursors to yield about 4 g of dried powder. Successive impregnations of different precursors were carried out when precursors were not miscible. The solids were heated at 723 K in nitrogen flow for 1 h. The loading of the primary metal was 0.5 wt% for Rh, Pt and Pd and 4 wt% for Ni. The amount of secondary element could take two levels (high or low corresponding to element II/element I molar ratio = 2.64 and 0.66, respectively). The alumina supports were sieved (250-360 μm) before impregnation.

TABLE 2
Convention for sample naming

Name	Support	Metal I	Metal II	Metal II loading (wt%)
ANiSn0.07S	A (δ-alumina)	Ni	Sn	0.07
BNiSn0.2S	B (θ-alumina)	Ni	Sn	0.2
BPd	B (θ-alumina)	Pd	-	-

Table 2 gives some examples of the nomenclature used to name the samples.

The whole library of catalysts has been tested on HT rig for hydrogenation of *o*-xylene and isomerisation of 3,3-dimethyl-1-butene. Only a fraction of this library has been tested for *n*-decane dehydrogenation.

2.2 Parallel Reactors for HT Screening

A proprietary 16 channel-multitubular reactor which is now commercialized as the SWITCH 16 reactor system by *AMTEC GmbH* [21], was adapted for the *o*-xylene hydrogenation and for the 3,3-dimethyl-1-butene isomerisation reactions. The fluidic supply consists of a combination of two separate feed delivery modules and two 16-port valves which are placed before and after the multi-channel reactor array. This system offers the opportunity to feed one selected reactor with one particular feed composition (feed 1) while the 15 others are fed with a second composition (feed 2), which can be identical to or different from feed 1. This design has several advantages regarding testing capabilities and the type of experiments which can be carried out, *i.e.* it is possible to evaluate catalysts under exactly the same ageing period and more specifically to measure the initial activity of each catalyst. Testing conditions can be varied in the selected channel while the other channels are maintained under standard or inert conditions. In addition, catalyst deactivation can be measured in the selected channel while the 15 other channels are being regenerated [22]. Finally, this design ensures very accurate and reproducible flows in the selected channel by the 16-port valve.

The *n*-decane dehydrogenation reaction was performed on another sixteen reactors unit, the Spider unit. Details about the Spider unit are provided in the article by C. Bouchy *et al*. [23].

2.3 Hydrogenation of *o*-Xylene

Mixtures of *o*-xylene (*Fluka*, purissim p.a., ≥99%) and heptane (*Riedel-De Haen*, purissim p.a., ≥99%) used as diluent (1:9 wt ratio) were supplied by a syringe delivery system. The *o*-xylene contains less than 0.5% wt of *cis*- and *trans* 1,2-dimethylcyclohexane (DMCH) as impurities. Gas Chromatography (GC) analysis was performed by using an *Agilent* 3000 version QUAD instrument equipped with a four channel module. Channel A was used for hydrogen, nitrogen measurements (MolSieve 5A, BF PPU Plot, with Ar as carrier gas). Channel C was used for cis- and trans-dimethylcyclohexane (OV1) and Channel D for *o*-xylene quantification (Stabilwax). Each GC analysis was duplicated. Catalysts were preliminarily reduced under hydrogen at 673 K during 2 h.

Kinetic parameters are estimated against a set of experimental results obtained under 20-30 different operating conditions for temperature and hydrogen partial pressure. They are iteratively calculated by integrating the kinetic equation on the catalytic bed length and looking for convergence with the experimental results. Impact of *o*-xylene partial pressure p_{oX} on the conversion was minimal compared to hydrogen partial pressure p_{H_2}. In order to accelerate the acquisition of data, p_{oX} was set to be constant resulting into having adsorption enthalpy of *o*-xylene ΔH_{oX} to be held as a constant too. ΔH_{oX} was set to be equal to −70 kJ/mol [24].

The modelling parameters of *o*-xylene hydrogenation come in two types: type I's are related to the conversion *i.e.* $ln\ A_{cis}$, $ln\ A_{trans}$, E_{cis}, E_{trans}, $ln\ S_{H_2}$, $ln\ S_{oX}$, H_{H_2}, n_{cis} and n_{trans}. Type II's are used to describe selectivity *i.e.* $ln\ A_{cis} - ln\ A_{trans}$, $E_{cis} - E_{trans}$, H_{H_2}, $n_{cis} - n_{trans}$.

2.4 Isomerisation of 3,3-Dimethyl-1-Butene

Mixture of 33DMB (*Fluka*, purissim p.a., ≥99%) is supplied by a syringe delivery system and vaporized in a CEM system (*Bronkhorst*) with nitrogen as carrier gas. Gas Chromatography (GC) analysis is performed by using an *Agilent* 3000 version QUAD instrument equipped with a four channel module. Channel A was used for H_2, N_2, measurements (MolSieve 5A, BF PPU Plot, with Ar as carrier gas). Channel C (OV1) and Channel D (Stabilwax) are used to analyse 3,3-dimethyl-1-butene (33DMB), 2,3-dimethylbut-1-ene (23DMB1), 2,3-dimethylbut-2-ene (23DMB2). Each GC analysis was duplicated.

TABLE 3
Typical operating conditions of an *n*-decane dehydrogenation test on the Spider

Step	Targeted testing conditions	Observations
Reduction	2.7×10^{-6} Nm^3/s H_2 / reactor (10 NL/h H_2 / reactor) – 3 bar absolute – temperature increase 5 K/min one hour at 723 K	
Catalyst stabilisation	T = 733/743/753/763 K WHSV(n-C_{10}) = 60/160/240/340 h^{-1} – 3 bar absolute – H_2/n-C_{10} = 6 mol/mol	The temperature indicated is the unit regulation temperature – 3 analyses / reactor / operating condition – 1 h / operating condition
Catalytic data acquisition	T = 733/743/753/763 K WHSV(n-C_{10}) = 60/160 /240/340 h^{-1} – 3 bar absolute – H_2/n-C_{10} = 6 mol/mol	The temperature indicated is the unit regulation temperature – 3 analyses / reactor / operating condition – 1 h / operating condition

In refining and petrochemicals applications, in the case of bifunctional or monofunctional metal reactions in wich Pt, Pd or Ni are often used, the catalysts usually do operate after a reducing treatment generally performed in high temperature conditions under hydrogen. In addition Martin and Duprez [16] have shown that very significant changes in the acidity of catalysts such as Rh and Pt on Al_2O_3 are noticed after reduction treatment under hydrogen. In order to characterize catalysts in conditions approaching the industrial cases, we have chosen to reduce all the catalysts under hydrogen flow at 400 °C for 2 h.

In order to determine the optimum screening temperature, a first screening of a few samples at various temperatures ranging from 483 to 563 K was performed and the temperature of 533 K was retained for all other tests. The reaction feed is composed of 1% wt *n*-octane – 99% wt 3,3-dimethyl-1-butene (μ = 650 $kg.m^{-3}$) under nitrogen. Liquid flow is fixed to 1.6×10^{-10} m^3/s (0.6 $mL.h^{-1}$), nitrogen flow to 8.3×10^{-9} m^3/s (30 $mL.min^{-1}$), hence p_{33DMB} equals 0.06 bar. In order to evaluate the impact of the deactivation on the acidity, all catalysts were tested twice at 5 and 30 minutes of time on stream.

As the reaction is sensitive to acid features, the activity can vary of by several magnitude orders from one catalyst to the other. Therefore, for a fixed operating condition (temperature, partial pressures and contact time), a significant number of catalysts exhibits conversion higher than 30% (too high for proper activity evaluation) or lower than detection limits. An initial HT screening has been carried out with a liquid hourly space velocity (LHSV) of 1.95 h^{-1} corresponding to a catalyst loading of 200 mg in order to evaluate the level of conversion. The catalysts falling outside the above mentioned limits were tested a second time with an adjusted LHSV (7.8 h^{-1}, 3.9 h^{-1}, 1.3 h^{-1}) corresponding to loadings of 50, 100, 300 mg respectively.

As described earlier the descriptor of acidity (r_{iso}) is calculated as the rate of a 1st order reaction at the same 33DMB partial pressure (0.06 bar).

2.5 *n*-Decane Dehydrogenation

One should note that production of olefins and diolefins is limited by thermodynamic equilibrium as production of shorter hydrocarbons resulting from cracking and hydrogenolysis is not. Therefore selectivity towards the different products is extremely dependent on how operating conditions get the system close to thermodynamic equilibrium of the paraffin *versus* olefin reaction. Contact time is varied from one catalyst to the other to obtain the relevant conditions.

On the Spider reactor, 50 mg of catalytic material diluted in SiC is tested with *n*-decane mixed with 500 ppm of water. The typical operating conditions of an *n*-decane dehydrogenation test on the Spider are described in Table 3.

A simple kinetic model was used to compare catalysts under similar operating conditions because the temperature of the rig was different from one reactor to the other (maximal gap of approx. 8 K). More details about this kinetic approach can be found elsewhere in this special issue.

Using the model, all products yields can be regressed to the same operating conditions at different contact time:
- total pressure = 2.7 bar;
- reaction temperature = 743 K;
- molar ratio H_2/nC_{10} = 6.

The performance indicator chosen for the complex reaction is the initial productivity *i.e.* the initial slope of the yield *versus* contact time. The initial productivity of the catalyst for olefin, aromatics and cracked/isomerised products (respectively noted *Ol*, *Aro* and C_{10-}) are regressed against the descriptors of the hydrogenation of *o*-xylene and the descriptor of acidity r_{iso}.

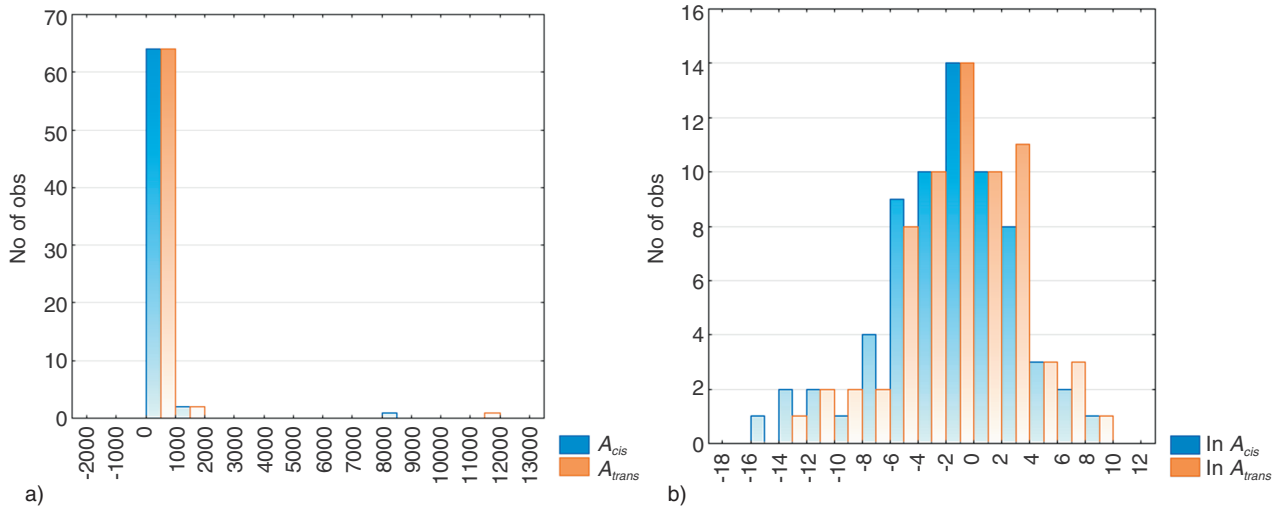


Figure 3

Distribution of pre-exponential factors and its "normalisation" on logarithmic scale. a) Distribution of factors A_{cis} and A_{trans}; b) Distribution of descriptors *ln* A_{cis} and *ln* A_{trans}.

3 RESULTS

3.1 Catalyst Descriptors from *o*-Xylene Hydrogenation

Descriptors for hydrogenation of *o*-xylene are the kinetic parameters. As mentioned earlier kinetic parameters can be combined in two sets: one to describe activity, the other for selectivity. Descriptors are following the same trend and are divided in type I and type II.

However, due to the nature of the equations, pre-exponential factors (A_{cis}, A_{trans}, S_{oX} and S_{H_2}) are exponentially distributed (*Fig. 3a*). In order to get a more "normal" distribution (*Fig. 3b*), we use the logarithmic descriptors *ln* A_{cis}, *ln* A_{trans}, *ln* S_{oX} and *ln* S_{H_2}.

The main statistics of the descriptors are detailed in Table 4.

Average and median values are similar. This is an indication that each parameter distribution is fairly symmetrical. The amplitude for pre-exponential/entropy type of factors as well as for type ones (activation energy and enthalpy) is very wide. These parameters have a large standard deviation compared to their average value. It means that the catalysts show a very wide variety of kinetics behaviour which indicates a large diversity of catalytic properties among the material library.

Maximum order for hydrogen partial pressure is around 3, as expected. The kinetic equation is modelled for the dissociative adsorption of three hydrogen molecules. The parameter n_i (subscript i stands for either *cis* or *trans*) is an indication of the sensitivity of the reaction to these adsorptions: with n_i close to 0, the reaction rate is insensitive to hydrogen partial pressure; with n_i close to 3, the three adsorption steps can be considered as rate determining steps.

Descriptors were built from Principal Components Analysis (PCA) of the kinetic parameters (*Fig. 4*). PCA is applied to type I & II descriptors separately. Considering the variable space described by the descriptors of each type, PCA is a mathematical method that builds a new, smaller set of variables – the Principal Components (PC) – describing the same space but the variability – measured by the statistical variance of the variable – of each PC has been optimised. In other words the new set of variables concentrates most of the variability of the previous set in fewer variables. Furthermore PC are uncorrelated.

3.1.1 Principal Components for Type I Descriptors

From PCA statistical analysis, we found that three PC (1 to 3) are enough to gather around 90% of the variability of the dataset.

In Figure 5, the points indicate where the kinetic parameters are positioned in the plane delimited by various PC. The closest those points are from the red circle, the more the parameter contributes to the displayed PC. In Figure 5a, all the points seem close to the circle which means all the variables contribute significantly in PC 1 and 2. This is expected because these two PC concentrate around 75% of the variance of the system. In other

TABLE 4
Main statistics of *o*-xylene hydrogenation descriptors

	Unit	Average	Median	Min	Max	σ		
$ln\ A_{cis}$	-	−1.67	−1.64	−15.40	9.03	4.89	Type I	
$ln\ A_{trans}$	-	−0.97	−1.25	−12.50	9.34	4.40		
E_{cis}	kJ/mol	275	272	14	723	113		
E_{trans}	kJ/mol	261	254	15	640	101		
$ln\ S_{oX}$	-	6.41	7.04	−3.79	15.93	3.24		
n_{cis}	-	1.74	1.65	0.82	3.26	0.54		
n_{trans}	-	1.62	1.55	0.61	2.93	0.51		
$ln\ S_{H_2}$	-	3.17	3.19	−5.64	8.95	2.50		Type II
H_{H_2}	kJ/mol	−204	−211	−376	−50	63		
$ln\ A_{cis} - ln\ A_{trans}$	-	−0.70	−0.53	−4.25	0.84	0.85		
$E_{cis} - E_{trans}$	kJ/mol	13	13	−98	166	44		
$n_{Cis} - n_{Trans}$	-	0.12	0.13	−0.37	0.66	0.19		

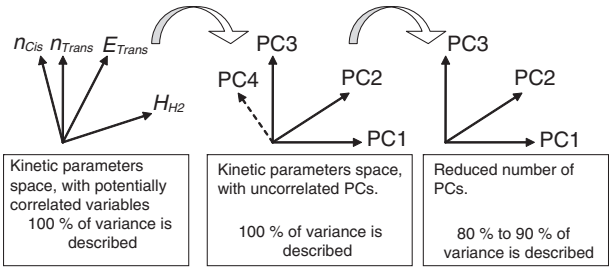


Figure 4
PCA steps.

words PC 1 and 2 capture 75% of the variability of the nine kinetic descriptors.

To understand what the main contributors for a specific PC are, we are looking to the closest points to the PC axis. On the same chart (*Fig. 5a*), the X axis is the PC 1 axis. The most important contributors in PC 1 are therefore the energies E_i, the orders n_i and the pre-exponential factors $ln\ A_i$.

Parameters are correlated when they stand close from the circle and close to each other. Therefore E_{cis} is correlated with E_{trans}, they are both correlated to lesser extent to entropy $ln\ S_{H_2}$, n_{cis} is correlated with n_{trans} and $ln\ A_{cis}$ with $ln\ A_{trans}$. Parameters are anticorrelated when they stand close from circle but are diametrically opposed. Entropy $ln\ S_{H_2}$ and energies E_i are anticorrelated with pre-exponential factors $ln\ A_i$. Parameters close from the circle are uncorrelated when they are perpendicular to each other as the pre-exponential factors $ln\ A_i$ are with H_{H_2}.

The same way each catalyst has a set of kinetic parameters values, it also has a set of PC values. Figure 6 shows the values of PC 1 and 2 for the catalysts library.

One can clearly see the strong influence of rhodium catalysts on PC1 as the points are spread along the X axis. This means that rhodium catalysts have shown the strongest diversity in their kinetic behaviour and PC1 captured exactly that. As for the second PC, the chart does not show any cluster of catalysts: primary metal does not explain how catalysts may have contributed in a specific way to PC2. The same goes for PC3 (not illustrated).

3.1.2 Principal Components for Type II Descriptors

Applying the same method to the five type II descriptors, it appears that three PC contain more than 95% of the information (*Fig. 7*).

Energy parameter $E_{cis} - E_{trans}$ is anticorrelated with pre-exponential parameter $ln\ A_{cis} - ln\ A_{trans}$.

Energy parameter $E_{cis} - E_{trans}$ is well correlated with order parameter $n_{cis} - n_{trans}$. This means that catalyst with a great difference between E_{cis} and E_{trans} is very likely to have a great difference between n_{cis} and n_{trans}.

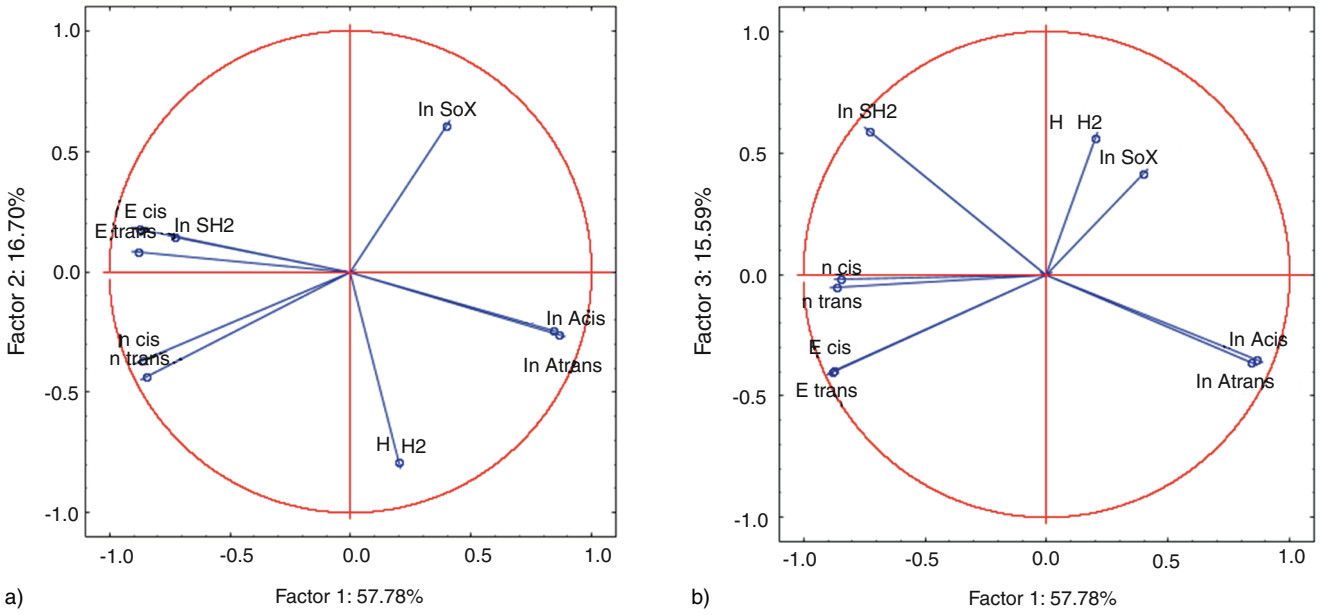


Figure 5

Type I kinetic parameters contribution in PC. Percentage in the axis legend indicates the amount of variability captured by the corresponding PC. a) Projection of kinetic parameters on 1st and 2nd PC plane; b) Projection of kinetic parameters on 1st and 3rd PC.

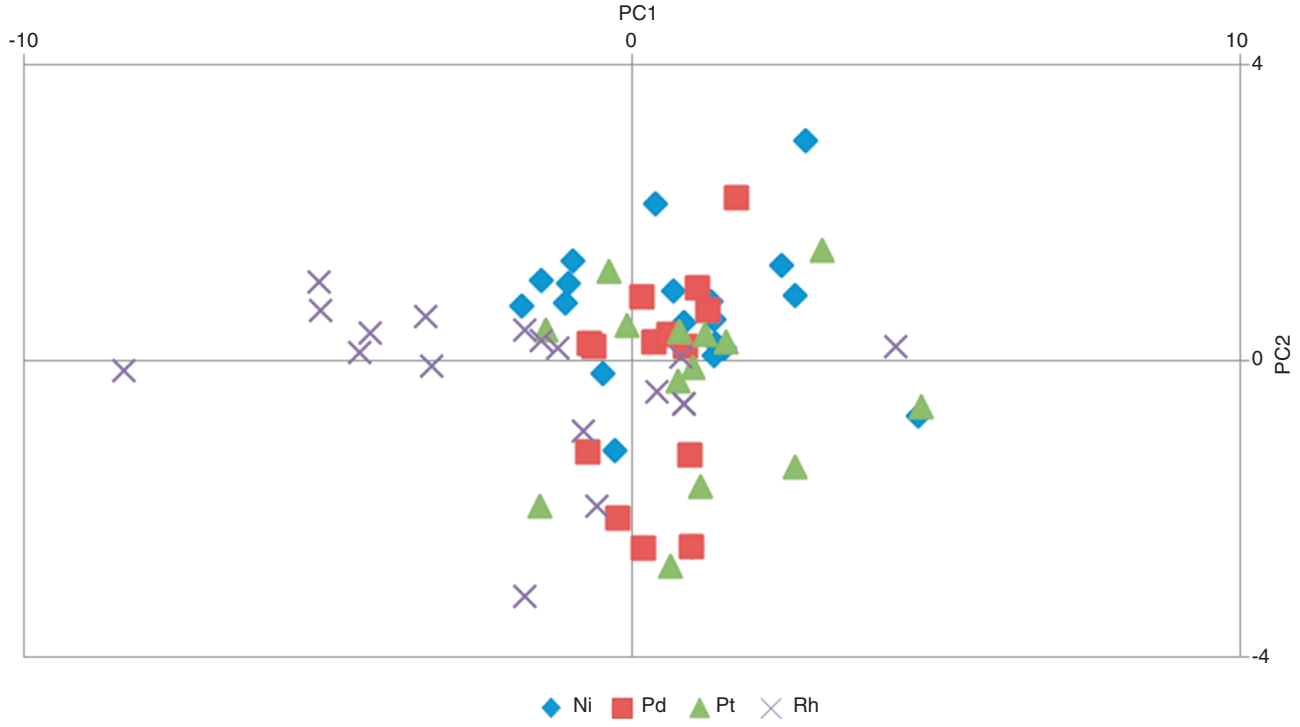


Figure 6

Type I PC values for the catalysts library. Each point represents a different catalyst. Series are based on the catalyst primary metal.

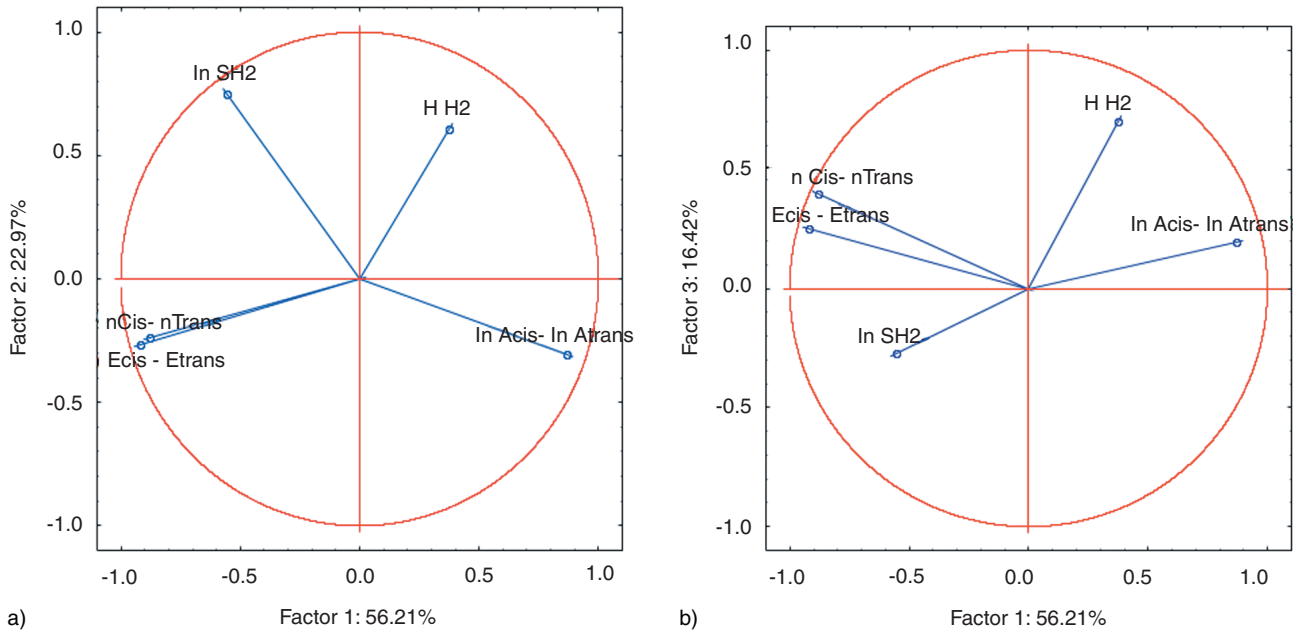


Figure 7

Type II kinetic parameters contribution in PC. Percentage in the axis legend indicates the amount of variability captured by the corresponding PC. a) Projection of kinetic parameters on 1st and 2nd PC plane; b) Projection of kinetic parameters on 1st and 3rd PC.

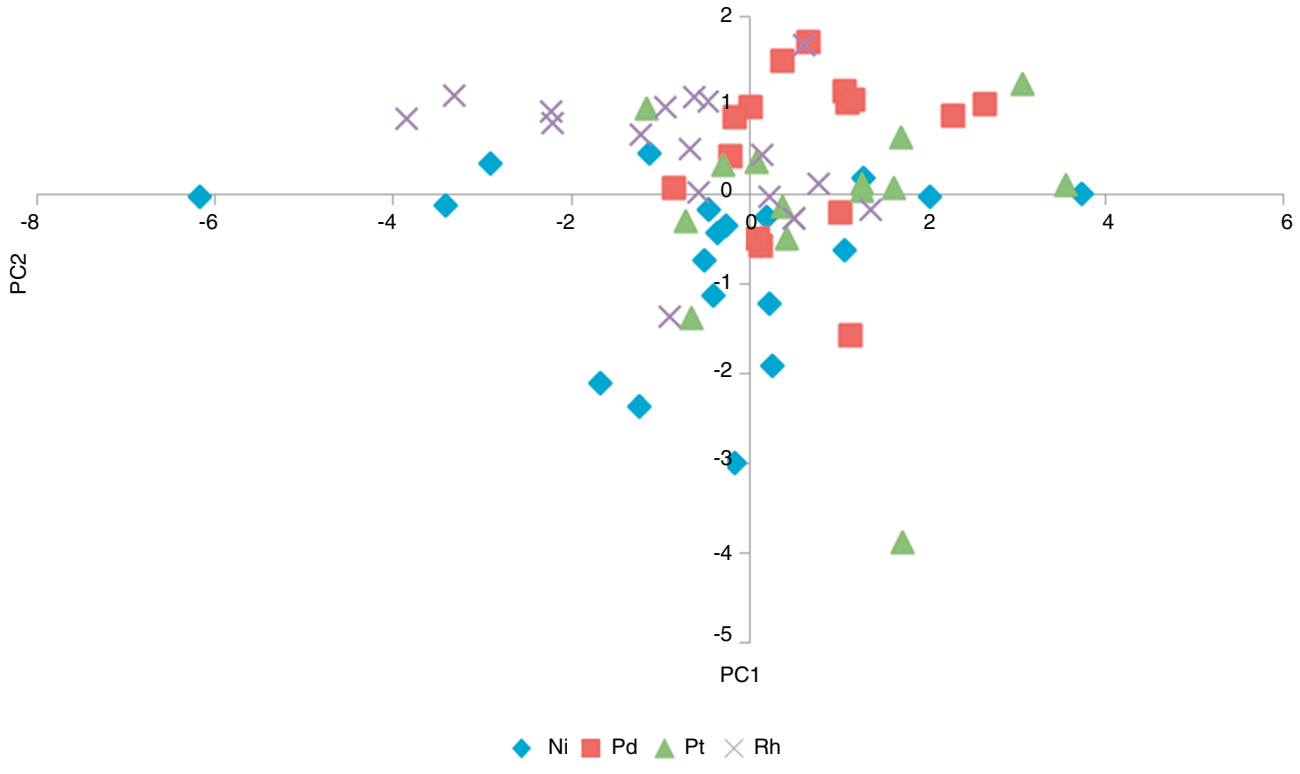


Figure 8

Type II PC values for the catalysts library. Each point represents a different catalyst. Series are based on the catalyst primary metal.

Adsorption energy H_{H_2} is uncorrelated with Energy parameter $E_{cis} - E_{trans}$ and $n_{cis} - n_{trans}$.

PC coordinates of the catalysts library are charted in Figure 8 for PC 1 and 2. The plot colour indicates the primary metal of each catalyst.

There is no real cluster standing out in Figure 8 or in PC1 *versus* PC3 chart (not illustrated). Nickel catalysts show the widest range of diversity, which is why they are predominant in the formation of PC1 and PC2. The other primary metals are packed together and have similar influence in the construction of the main PC.

3.2 Catalytic Descriptor for Isomeration of 3,3-Dimethyl-1-Butene

Results have been published elsewhere [17]. Catalyst acidity has been measured by the mean of their activity rate for the isomerisation reaction. The recorded ranking is reported in Figure 9, by decreasing acidity. The isomerisation activity is essentially due to the type of support of the catalyst: most of the catalysts supported on δ-alumina and the support itself are on top of the list whereas θ-alumina and the associated catalysts are usually lower ranked. The presence of metallic isomerisation would increase of more than one order of magnitude the measured activities of the support but this only had been observed for Mo catalysts, which are well known to generate supplementary Brønsted sites [17]. Otherwise the presence of metal results either in less significant increase of activity (Pt, Pd) or more or less significant decrease of activity (Ni, Rh, Mn).

The catalysts naming convention is illustrated in Table 2 with few examples as a reminder.

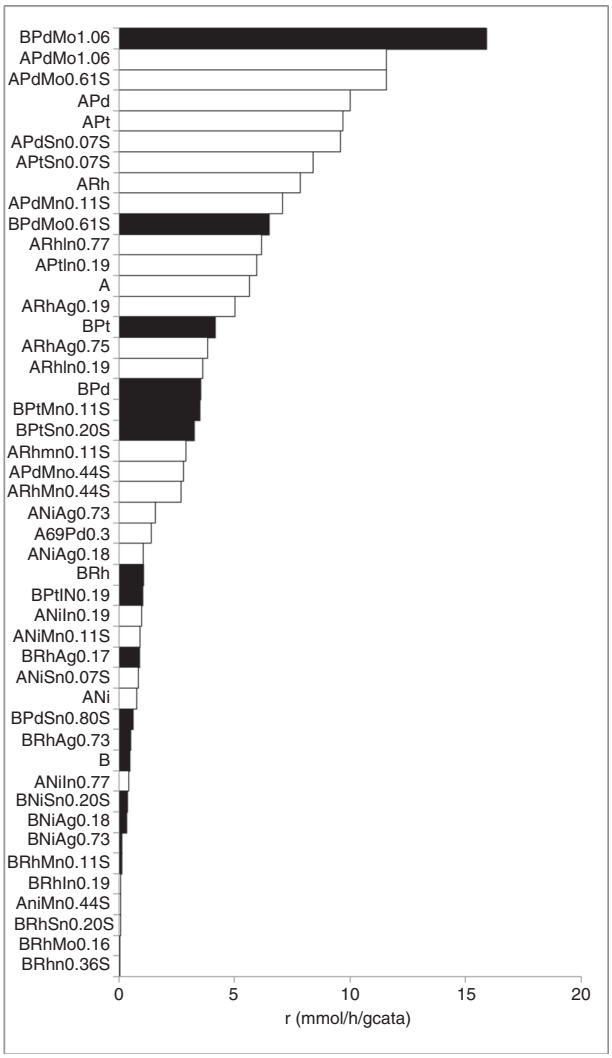


Figure 9

Activity rate for the isomerisation of 3,3-dimethyl-1-butene. Bars are coloured following the type of support. Black: θ-alumina; white: δ-alumina.

3.3 Results for the *n*-Decane Dehydrogenation Reaction

Olefins, aromatics and cracked/isomerised products yields are plotted *versus* contact time on Figure 10 for all the catalysts. More details about the kinetic approach are provided in the article by C. Bouchy *et al.* [23].

Comparison of the different catalysts is mostly relevant when thermodynamics effects are negligible. This is why the initial productivity i.*e.* the initial slopes of the yield in olefins, aromatics and cracked products (respectively named *Ol*, *Aro* and C_{10-}) has been retained to be the indicators of the performance of the catalysts.

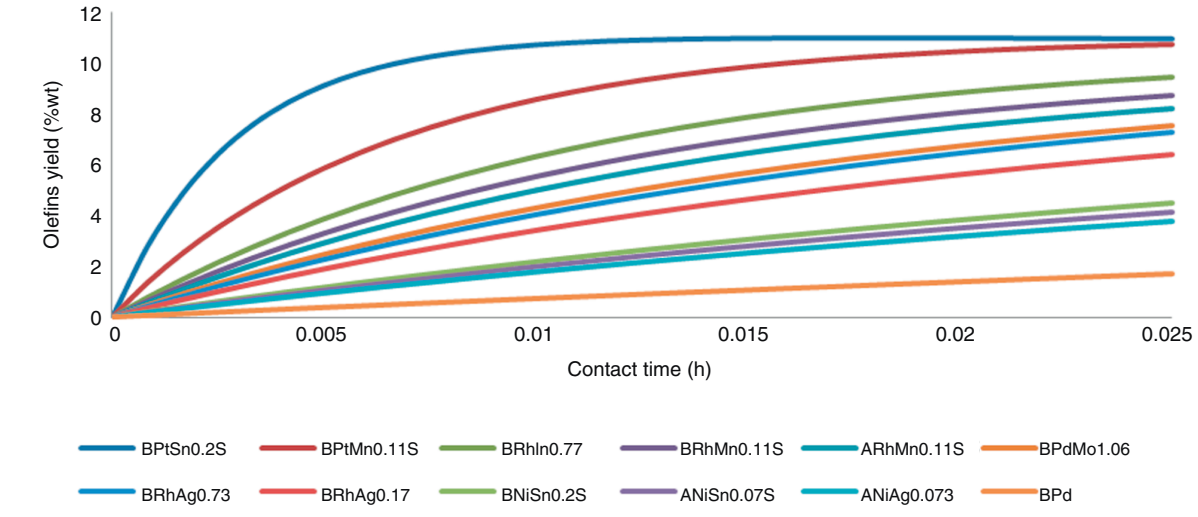
The productivities for each product type are displayed in Table 5 for all the samples.

If the primary goal of this work is to try to model these performance indicators, it is nonetheless fruitful to use them to compare the performances of the catalysts. To make them comparable they are normalised. Normalised values P_{norm} of the performance P are given by the following equation and are presented in Figure 11:

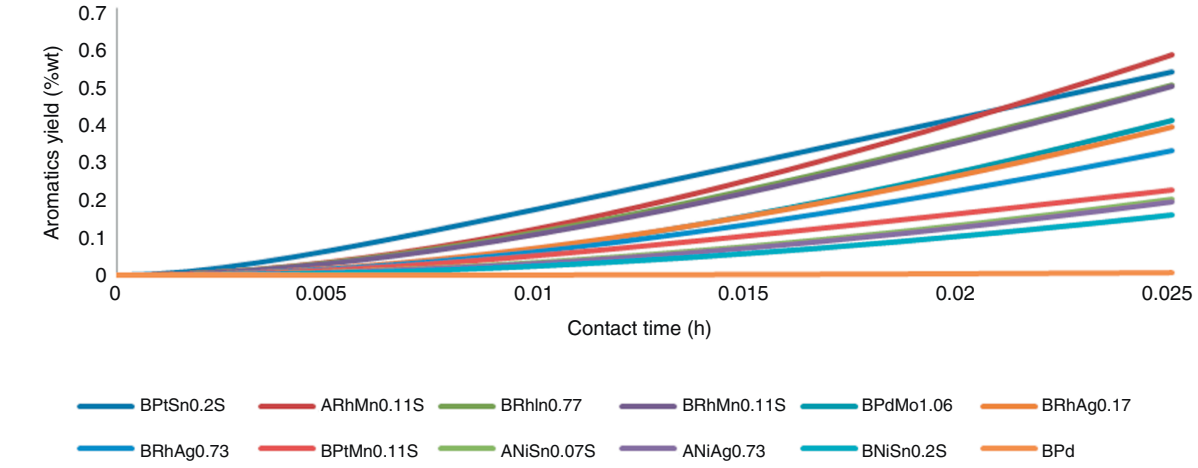
$$P_{norm} = \frac{P - \overline{P}}{\sigma^2}$$

where $\overline{P}$: mean of descriptor on all catalysts for each type of productivity; σ^2: standard deviation of descriptor on all catalysts for each type of productivity.

Positive values of P_{norm} are performances above the average, negative are below average. This approach gives a ranking of the catalysts for each type of productivity



a)



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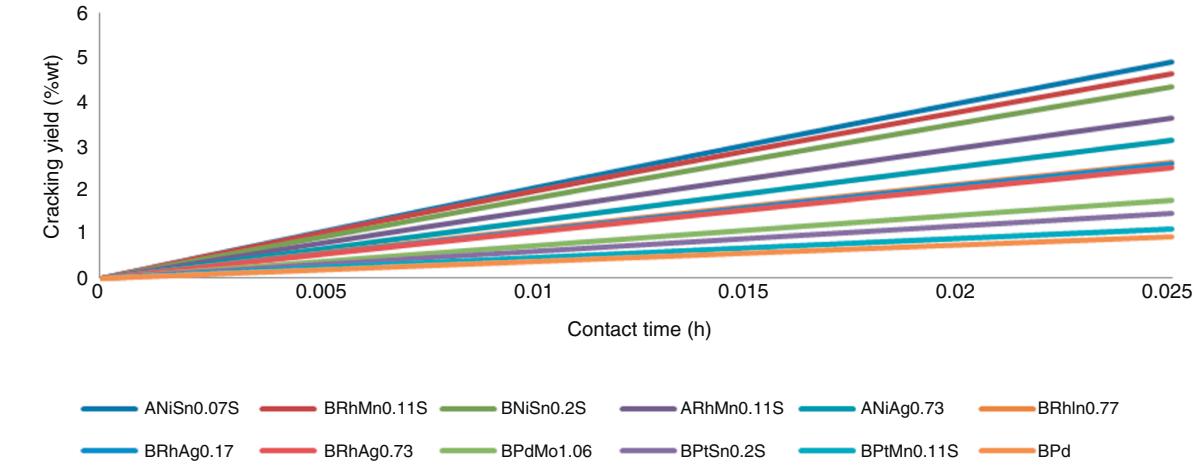

c)

Figure 10

Yield in a) olefins, b) aromatics and c) cracked products. Note: catalysts in legend are sorted by decreasing initial rate.

TABLE 5
Values of initial productivity in olefins, aromatics and cracked products

Sample	Olefins (*Ol*) %wt/h	Aromatics (*Aro*) %wt/h	Cracked products (C_{10-}) %wt/h
ANiAg0.73	199	6.0	127
ANiSn0.07S	223	6.2	198
BNiSn0.2S	248	4.9	176
BPd	78	0.2	38
BPdMo1.06	545	12.8	71
BRhAg0.17	408	12.4	105
BRhAg0.73	492	10.6	101
ARhMn0.11S	646	19.3	148
BRhMn0.11S	736	16.7	189
BRhIn0.77	878	17.0	107
BPtMn0.11S	1 461	7.6	45
BPtSn0.2S	2 729	20.1	60

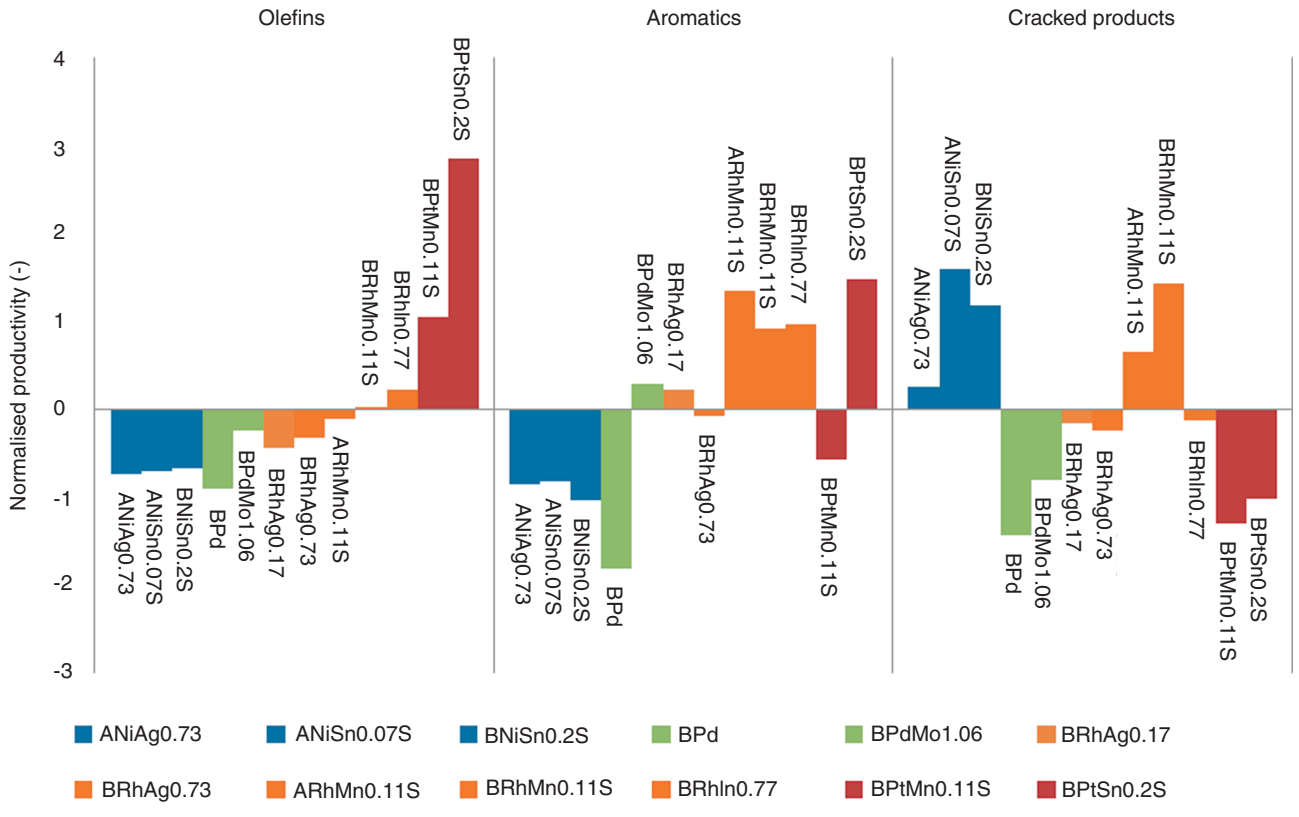

Figure 11
Normalised values of performances (no dimension). Blue: Ni catalysts; green: Pd catalysts; orange: Rh catalysts; red: Pt catalysts.

TABLE 6
Modelling of performances: variables, R^2 and p-values. Values in red are below the arbitrary significance level (5%)

CR performance	R^2	Model variables	p-value	Outlier
Ol	0.68	APC #2	0.0009	BRhAg0.73
Aro	0.62	APC #1	0.05	BRhAg0.73
		APC #2	0.05	
		APC #3	0.85	
		r_{iso}	0.39	
C_{10-}	0.60	SPC #3	0.01	ANi
		r_{iso}	0.03	

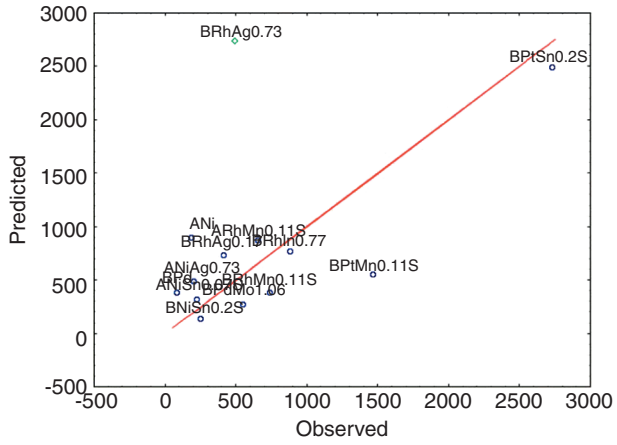

Figure 12

Observed *versus* predicted values for performance *Ol*. Model is built without BRhAg0.73 values.

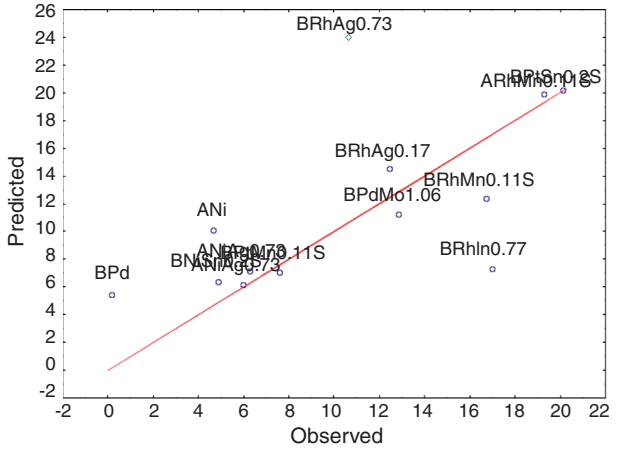

Figure 13

Observed *versus* predicted values for performance *Aro*. Model is built without BRhAg0.73 values.

but also a rough idea how far is the performance of a catalyst from the library average. It is here possible to evaluate how a catalyst performed in terms of olefins, aromatics productions and cracking comparatively to the others and to try to find some patterns or unexpected results.

Ni catalysts show a consistent behaviour over the three types of reaction (dehydrogenation, aromatisation and cracking): they produce low levels olefins and aromatics but high levels of cracked products (compared to the other samples), even though catalysts were stabilised. The type of primary metal of the other catalysts (Pd, Rh, Pt) does not explain as well their behaviour. The influence of other second metals and of the support may be less significant on Ni catalyst because they are loaded to 4%wt instead of 0.5%wt for the other catalysts primary metal.

Pt catalysts show significantly higher initial rate of dehydrogenation and lower cracking performance.

BPd is showing the lowest productivities (compared to the other samples). It may be due to the fact that a low amount of metal is supported on a low surface area alumina. By adding molybdenum as a secondary metal to palladium the catalyst is raised to be average for the three types of reaction. Molybdenum loading is significantly higher than platinum's (1.06%wt *vs* 0.5%wt) and probably modifies the structure of the active sites in depth.

Amongst Rh catalysts, those promoted with manganese show the most consistent behaviour: they easily

crack *n*-decane and produce high levels of aromatics but their dehydrogenation productivity is just average (compared to the other samples).

3.4 Modelling of *n*-Decane Dehydrogenation Reaction Performances

Note: Principals Components (PC) calculated from type I parameters (*Tab. 4*) are named *APCs* (PC for activity kinetic parameters); PC for type II parameters are named *SPC* (PC for selectivity kinetic parameters).

Given the limited number of data points, it is critical to build models with few variables. Therefore, the task here is to minimize the number of variables and it has been done to the expense of the model fitting. Various multilinear models involving the different principal components have been investigated but it is fair to mention that the complete dataset could not be correctly modelled because of outliers. They were excluded to reach the results below.

Table 6 summarises the main results.

The *p*-value gives the probability that the effect of the variable on the model is actually purely accidental or in other words, the lower the probability the more meaningful the variable is in the model. It is usually agreed that the variable is significant when its *p*-value is under 0.05.

It appears that performance *Ol* is well correlated with APC #2 (R^2 = 0.68) when BRhAg0.73 is considered as an outlier. Figure 12 shows observed *versus* predicted values.

The model is heavily biased by BPtSn0.2S but it is not enough to explain the correlation between APC2 and *Ol*. Figure 13 shows that the model strongly overestimates the value for the outlier BRhAg0.73.

Performance *Aro* is modelled after APCs 1 to 3 and the acidity descriptor *rISO* (R^2 = 0.62). BRhAg0.73 can be regarded as an outlier.

The *Aro* values are more evenly distributed than for *Ol* and the weight of BPtSn0.2S is no longer there to guide the model in a certain direction. Therefore, the model is having more variables for a lower coefficient of determination. However, if not perfect the model defines a trend supported by significant variables ($p <$ 0.05 for APC1 and APC2).

Performance C_{10-} is modelled with variables SPC #3 and the acidity descriptor r_{iso} (R^2 = 0.60) when considering ANi as an outlier.

Figure 14 shows that the models underestimates catalyst ANi's performance C_{10-}. SPC3 and r_{iso} are significantly connected to performance C_{10-}.

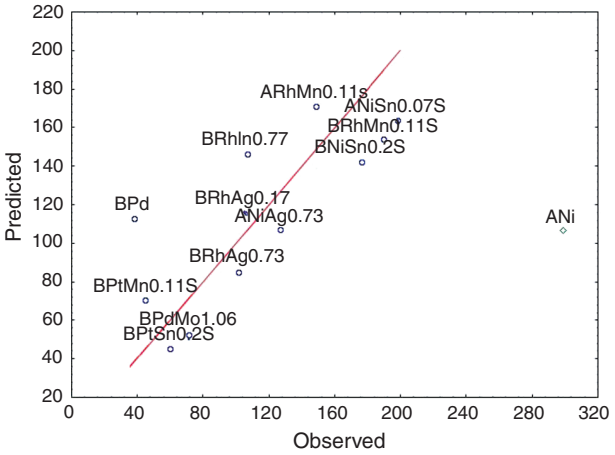

Figure 14

Observed *versus* predicted values for performance C_{10-}. Model is built without ANi values.

4 DISCUSSION

Models using kinetic parameters (plus r_{iso}) are not reported here. They were better fitting but the model variables were not statistically significant. This was essentially because there were too many of variables compared to the number of points to model. In other words with that many variables in the model, it would be possible to model any performances. Therefore, it was critical to bring down the number of variables with the help of the PCA. The models are still correct though not perfect and they use statistically significant variables. Furthermore having fewer variables helps to get a more meaningful model.

There is a correlation between APC2 and *Ol* (*Tab. 6*). But APC2 main contributors are the H_2 adsorption enthalpy $H_{H_2}$and to a lesser extent to *o*-xylene adsorption entropy *ln* S_{oX}. Hence it can be said that the olefins initial production rate *Ol* can be partially modelled by the contribution of the H_2 adsorption enthalpy $H_{H_2}$and to a lesser extent to *o*-xylene adsorption entropy *ln* S_{oX}.

Model of performance *Aro* with PCs is less efficient but the model retains APC1 and APC2 as significant variables. This result is consistent with the fact that *Aro* is correlated with *Ol* (coefficient of correlation = 0.62) therefore the models to describe both performances have to be similar. This also explains why APC2 is significant in both models.

Catalyst ANi was discarded to obtain a better model for C_{10-} but using PCs permitted to retain only significant parameters.

The production of olefins in the complex reaction is essentially occurring on metal sites. Therefore it was expected that hydrogenation descriptors, being representative of catalysis on metallic sites, will play an important role in the model. And this was confirmed by the strong correlation found between performance *Ol* and APC2.

Cracking in the complex reaction is supposed to be strongly dependent on the acidity of the catalyst. Therefore, isomerisation rate acting as the descriptor of acidity had to play a key role in modelling cracking performance. And this was confirmed when descriptor r_{iso} was found to be significant.

CONCLUSION

This work has validated the assumption that model reactions descriptors are representative of a catalytic function in complex reaction performances which can be seen as an extension of traditional QSAR approach.

The methodology goes through the following steps:

- selecting the relevant model reactions based on the chosen complex reaction by assessing the catalytic functions the model reaction need to describe;
- defining kinetic models and reaction parameters that can be relevant to describe the intrinsic catalytic properties involved in the mechanism of the complex reaction;
- building the descriptors by PCA from the set of kinetic parameters;
- modelling the performances of the complex reaction with the model reactions descriptors;

This work is setting the basis for a more systematic mapping of the catalytic properties through model reactions. This is especially relevant in the context of high throughput experimentation.

Library of diverse catalysts can be characterized by testing various model reactions. They can be regarded as a knowledge which can be later reused in a more general catalyst development strategy. Indeed key performance indicators for other industrial applications can use these descriptors to build new models and shorten product to market development times.

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