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Using High Throughput Experimentation Approach for the Evaluation of Dehydrogenation Catalysts: Potential Interests and Drawbacks

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Résumé — Utilisation d'une approche d'expérimentation à haut débit pour l'évaluation de catalyseurs de déshydrogénation: intérêt et limitations — Les mono oléfines linéaires longues de 10 à 14 atomes de carbone sont des intermédiaires pour la fabrication de produits détergents biodégradables. Industriellement ces oléfines peuvent être obtenues par déshydrogénation de paraffines longues sur des catalyseurs spécifiques de déshydrogénation dans des conditions opératoires appropriées. La phase active de ces catalyseurs est typiquement multimétallique, à base de platine modifié par un ou plusieurs promoteurs.

L'utilisation d'une approche par expérimentation à haut débit peut être d'un intérêt certain pour optimiser des formulations multimétalliques en raison, d'une part, du nombre croissant de formulations possibles avec la quantité d'éléments considérés et, d'autre part, de l'existence potentielle d'interactions non linéaires entre les éléments.

Cet article est ainsi consacré à la description des outils d'expérimentation à haut débit utilisés pour la préparation et l'évaluation catalytique en déshydrogénation du *n*-décane de catalyseurs modèle "Pt-Sn-X" supportés sur alumine ainsi qu'à la stratégie employée pour l'optimisation de formulation et les résultats expérimentaux obtenus au sein d'un espace d'étude prédéfini.

Une approche basée sur l'utilisation de plans d'expériences pour construire un modèle mathématique de prédiction a été mise en œuvre pour tenter d'optimiser la formulation de catalyseurs trimétalliques "Pt-Sn-X" au sein d'un espace d'étude défini. Cette approche n'a pas pu être menée à son terme car la variation des propriétés catalytiques en fonction des formulations catalytiques du plan d'expériences n'est pas assez importante par rapport à la variance expérimentale.

Les résultats obtenus ont cependant permis de vérifier un concept clé pour la maximisation de la sélectivité d'un catalyseur de déshydrogénation des paraffines longues. A iso-acidité résiduelle et dans l'hypothèse où la formation des coproduits met essentiellement en jeu des mécanismes bifonctionnels pour lesquels l'étape limitante se déroule sur la phase acide, la maximisation de la sélectivité va de pair avec la maximisation de l'activité de la fonction déshydrogénante du catalyseur.

Abstract — Using High Throughput Experimentation Approach for the Evaluation of Dehydrogenation Catalysts: Potential Interests and Drawbacks — Linear monoolefins with 10 to 14 carbon atoms are intermediates in the manufacture of biodegradable detergent products. These olefins can be obtained industrially by dehydrogenation of long chain paraffins on specific dehydrogenation catalysts under suitable operating conditions. The active phase of these catalysts is generally multimetallic, platinum-based modified by one or more promoters.

Use of a high throughput experimentation approach may be interesting to optimise multimetallic formulations due firstly to the increasing number of possible formulations with the number of elements considered and secondly to the possible existence of nonlinear interactions between the elements.

This article is therefore dedicated to a description of the high throughput experimentation tools used for preparation and catalytic evaluation during dehydrogenation of n-decane of alumina-supported “Pt-Sn-X” model catalysts, alongside the strategy used to optimise the formulation and the experimental results obtained in the predefined study domain.

An approach based on the use of design of experiments to build a mathematical prediction model has been implemented to attempt to optimise the formulation of trimetallic “Pt-Sn-X” catalysts within a defined study domain. This approach could not be completed since the variation of the catalytic properties depending on the catalytic formulations of the design of experiments is not large enough with respect to the experimental variance.

The results obtained nevertheless demonstrated a key concept to maximise the selectivity of a long chain paraffin dehydrogenation catalyst. At the same residual acidity and assuming that the formation of coproducts mainly involves bifunctional mechanisms for which the limiting step occurs on the acid phase, maximising the selectivity goes hand in hand with maximising the activity of the catalytic dehydrogenating function.

INTRODUCTION

Alkenes are key intermediate products for the petrochemical industry. Most biodegradable detergents are sulphonated derivatives of linear alkyl benzene compounds. These compounds are synthesised by alkylation of benzene by long chain linear monoolefins (generally 10 to 14 carbon atoms) under suitable operating conditions. These olefins can be prepared industrially by dehydrogenation of long chain paraffins on a specific dehydrogenation catalyst in a fixed bed reactor. Due to the thermodynamic constraints, the reaction is conducted at high temperature (typically 723-773 K) and low pressure (200-300 kPa) in the presence of hydrogen [1]. In addition to the formation of linear olefins, other undesired products such as diolefins, triolefins, aromatics, *iso*-paraffins, *iso*-olefins, cracking products and coke are also observed. A catalyst with maximum selectivity for the production of monoolefins is therefore required. Figure 1 shows the various reactions likely to occur on a catalyst during dehydrogenation of a long chain paraffin.

The active phase of industrial dehydrogenation catalysts is generally platinum-based modified by one or more promoters or chromium-based modified by promoters. The supports most frequently used are alumina-based doped with alkali metals, zinc or magnesium aluminate or zirconium oxide [2]. All residual acidity on the support must be limited in order to minimise reactions such as isomerisation and cracking. Use of promoters, for example tin for platinum-based catalysts, improves catalytic performance in terms of activity, selectivity and stability [3].

Use of a high throughput experimentation approach may therefore be interesting to optimise multimetallic formulations due firstly to the increasing number of possible formulations with the number of elements considered and secondly to the potential existence of nonlinear interactions between

the elements. This type of approach has therefore been implemented to attempt to optimise the formulation of trimetallic “Pt-Sn-X” model catalysts on an alumina support in terms of activity and selectivity for the production of olefins during dehydrogenation of a model molecule, *n*-decane. In fact, in the field of heterogeneous catalysis, the high throughput experimentation approach is not new and has already been applied by Mittasch *et al.* for the discovery of the first ammonia synthesis catalyst at the beginning of the last century [4]. Nowadays, this approach is of common use in the industry and academic groups are conducting fundamental research on various fields related to high throughput. More details can be found in recent and comprehensive reviews about high throughput techniques in heterogeneous catalysis [5-7].

The first section of this article is therefore dedicated to a description of the high throughput experimentation tools used for preparation and catalytic evaluation of catalysts and management of the associated data. The second section details the kinetic approach which has been developed and implemented to analyse the results of the catalytic tests. Lastly, the third section outlines the strategy used to optimise the catalyst formulation and presents the obtained experimental results.

1 OVERVIEW OF THE HIGH THROUGHPUT EXPERIMENTATION TOOLS AND WORKFLOW

1.1 Catalyst Synthesis

The catalysts were prepared by dry impregnation of an industrial support of preformed alumina, doped or not by an element X, then crushed and sieved to obtain a fraction in the size range 355-500 microns.

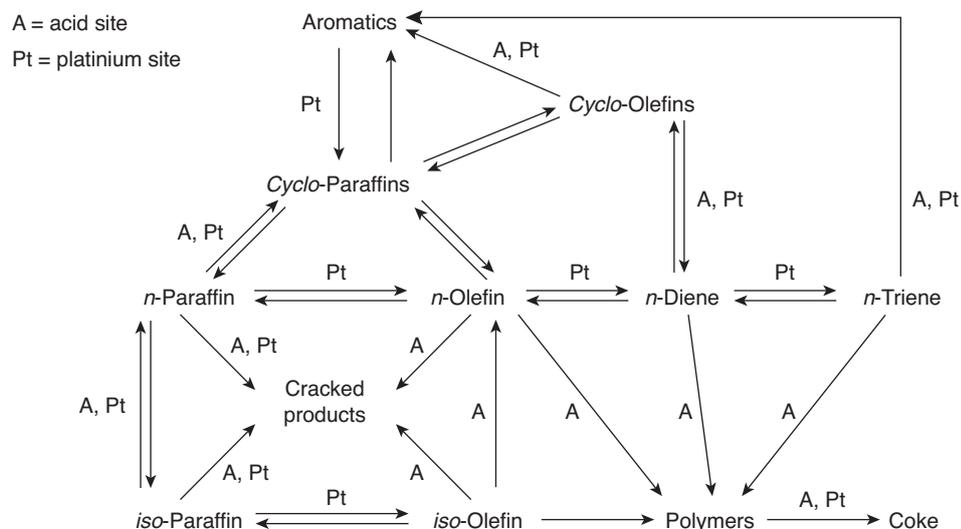


Figure 1

Reactions likely to occur during dehydrogenation of long chain paraffins on a platinum-based catalyst (according to [1]).

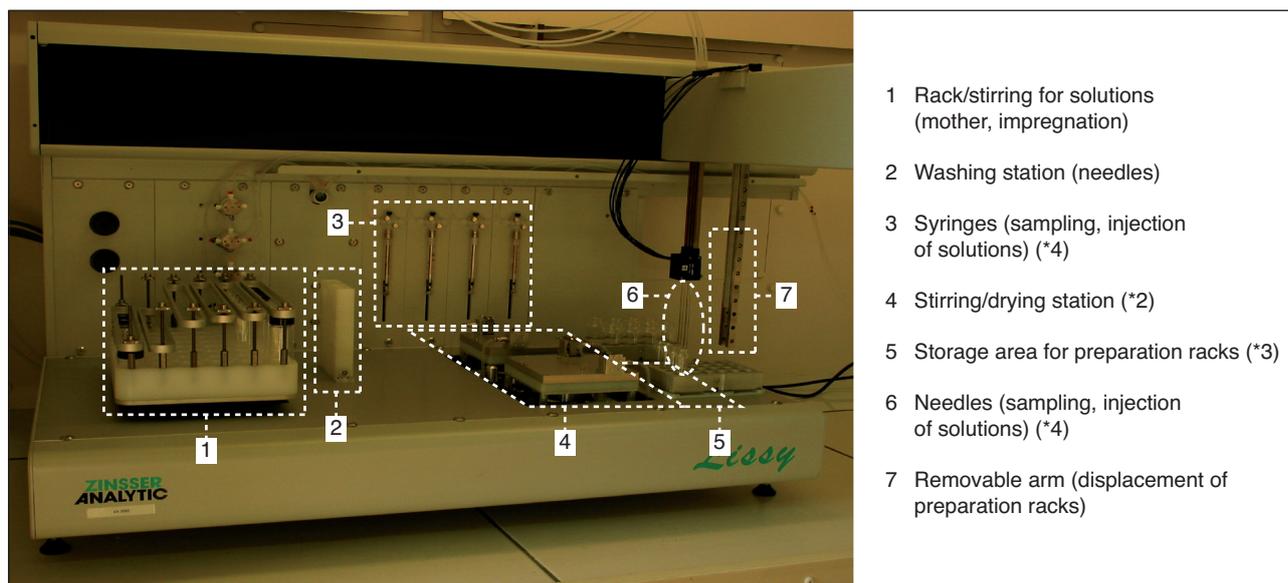


Figure 2

LISSY GXRL robot.

1.1.1 Impregnation Step

The dry impregnation steps are carried out on a LISSY GXRL robot manufactured by the Zinssep company (Fig. 2) which features a type of needle particularly suited to dry impregnation. The robot is used to prepare impregnation solutions from concentrated mother solutions, perform the dry impregnation step as such of typically one gram of

alumina support, and dry the impregnated solid. Typically, eight catalysts can be prepared in parallel on this tool.

1.1.2 Thermal Treatment Step

Calcination of solids (typically one gram) is carried out in fixed bed in an 8-reactor ERALY oven. A set of capillary tubes distributes the gaseous flow uniformly in the eight

TABLE 1
Dehydrogenation catalyst preparation protocol

Step	Objective	Implementation
1	Impregnation of tin and chlorine to obtain the same chlorine content	Dry co-impregnation, drying, calcination
2	Impregnation of platinum	Dry impregnation, drying, calcination

reactors. All reactors therefore receive the same thermal treatment.

1.1.3 Automated Synthesis of Dehydrogenation Catalysts

The protocol used to prepare the multimetallic catalysts of the study is applied by successive dry impregnations of tin then platinum on the alumina-support, doped or not by element X (*Tab. 1*). Tin impregnation is carried out by dry impregnation of an aqueous solution of tin dichloride SnCl_2 . Chlorine, in the form of hydrochloric acid, is added to the solution in order to adjust the residual chlorine content on the catalysts to 1% by weight before calcination and to obtain a comparable residual acidity level for all the catalysts. After impregnation, the solids are dried for 1 h 40 min at 100°C then transferred to the thermal treatment tool. The solids then undergo a calcination step under air (1 NL/h/gram of solid) for one hour at 520°C (temperature increase 5°C/min). The calcinated solids undergo a second dry impregnation step by an aqueous solution of hexachloroplatinic acid H_2PtCl_6 , before being dried and calcinated under the same conditions as the first step.

To ensure that the preparations obtained on our tools are reproducible, two formulations have been synthesised and characterised in addition to the design of experiments as

such: one poorly loaded with metals (0.1% Pt / 0.1% Sn / 1% Cl theoretical) and one highly loaded with metals (0.4% Pt / 0.5% Sn / 1% Cl theoretical). In addition, each synthesis is carried out four times using different preparation and calcination reactors to estimate the uncertainty associated with the automated preparation step. Table 2 lists for each catalyst the platinum, tin and chlorine contents measured by XRF (X-ray fluorescence) as well as the results of the double H_2/O_2 titration [8]. The measured element contents agree with the theoretical contents for the two formulations; the chlorine content is constant at about 0.8% for all catalysts, due to chlorine elution during the calcination steps. This constant value for the two catalysts in the design of experiments that are most and least loaded with metals shows that addition of hydrochloric acid during preparation is an efficient way of adjusting the chlorine content. The titration results are also consistent both as regards the first (V_1) and second (V_2) titration volumes, which shows that the dispersion state and the interaction between platinum and tin are similar for catalysts with the same theoretical formulation. These results demonstrate:

- good agreement between effective formulation and targeted formulation for a catalyst;
- that the overall dispersion state and the interaction between the metals are similar for catalysts with the same theoretical formulation;
- that the Cl content, and therefore the associated acidity level, is constant;
- good repeatability of the synthesis between the various synthesis reactors.

1.1.4 Catalyst Synthesis Data Management

Each prepared catalyst is recorded with a unique identification number in a company database. This database also includes,

TABLE 2
Characterisations of catalysts prepared on HTE (High-Throughput Experimentation) synthesis tools

Target formulation	0.1% Pt / 0.1% Sn / 1% Cl				0.4%Pt / 0.5% Sn / 1% Cl			
Reactors positions	1-1	7-7	1-1	7-7	1-1	2-2	7-7	8-8
Wt% Pt	0.08	0.10	0.09	0.10	0.39	0.39	0.39	0.38
Mean wt% Pt ± std deviation	0.09 ± 0.01				0.39 ± 0.01			
Wt% Sn	0.10	0.11	0.11	0.11	0.50	0.54	0.53	0.55
Mean wt% Sn ± std deviation	0.11 ± 0.01				0.53 ± 0.02			
Wt% Cl	0.81	0.82	0.83	0.85	0.86	0.86	0.87	0.85
Mean wt% Cl ± std deviation	0.83 ± 0.02				0.86 ± 0.01			
V_1 cc/g - H_2/O_2	0.04	0.05	0.06	0.07	0.36	0.37	0.38	0.37
V_1 mean ± std deviation cc/g	0.06 ± 0.01				0.37 ± 0.01			
V_2 cc/g - H_2/O_2	0.01	0.02	0.03	0.04	0.22	0.23	0.25	0.24
V_2 mean ± std deviation cc/g	0.03 ± 0.01				0.24 ± 0.01			

for each catalyst, its theoretical composition, the parameters associated with the synthesis and any characterisations made.

1.2 Catalytic Tests

1.2.1 Catalyst Tests Unit

The catalysts are evaluated on a catalytic test unit with sixteen fixed bed reactors, the Spider [9, 10]. Hydrocarbon feedstock, setpoint temperature and total working pressure are the same for all reactors. The gas and feedstock flowrates of each reactor are controlled individually. Temperature sensors (in the catalytic bed) and pressure sensors (upstream and downstream from the reactors) measure the operating values in real time for each reactor. Under the typical operating conditions of a dehydrogenation test (723-773 K) temperature differences of about 7 K are observed between the reactors. It is therefore impossible to compare the catalysts at equal temperature which means that, amongst other things, in view of the thermodynamic limitations inherent to the dehydrogenation reaction, a specific test protocol has to be developed (see Sect. 1.2.3).

1.2.2 On-Line GC Analysis System

The gaseous effluents from the unit are analysed on line by an Agilent 6890 chromatograph equipped with two FID

columns and analysers. The first column is used to analyse effluents from reactors 1 to 8 in turn and the second column effluents from reactors 9 to 16.

A traditional analysis of a *n*-decane dehydrogenation effluent typically lasts one hour, followed by 30 minutes for the chromatogram exploitation. These delays are incompatible with a high throughput evaluation of the catalysts and a fast, simplified analysis method was therefore developed for the Spider test unit. The various compounds in the effluent are classified into five families (Fig. 3):

- “cracked products” family for cracking and isomerisation products;
- “*n*-C₁₀” family for *n*-decane;
- “C₁₀ olefins” family for olefins with 10 carbon atoms;
- “C₁₀ diolefins” family for diolefins with 10 carbon atoms; and lastly
- “C₁₀ aromatics” family for aromatics.

With this simplified method, a dehydrogenation effluent can be analysed in two minutes.

1.2.3 Catalytic Test Protocol

Typically, 50 mg of catalyst of size 350-500 microns are mixed with carborundum of size 500 microns and loaded in the catalytic reactors. The heights of the catalytic beds are compatible with the hydrodynamic flow criteria [11] with a

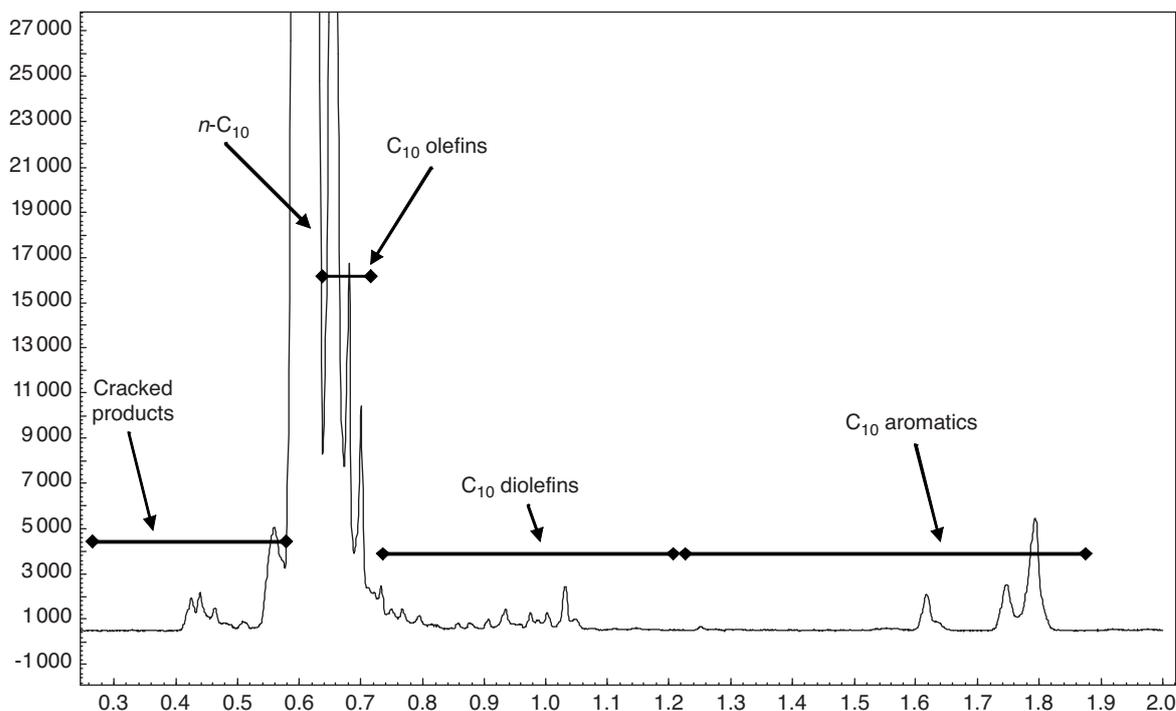


Figure 3

Example of chromatogram obtained with the method for fast analysis of a *n*-decane dehydrogenation effluent.

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

Step	Target operating conditions	Comments
Reduction	10 NL/h H ₂ / reactor 3 bar absolute temperature increase 5°C/min one hour at 723 K	The temperature indicated is the unit regulation temperature
Stabilisation under feedstock	WHSV(<i>n</i> -C ₁₀) = 60 h ⁻¹ H ₂ / <i>n</i> -C ₁₀ = 6 mol/mol 3 bar absolute 15 minutes at 733 K	The temperature indicated is the unit regulation temperature
Catalytic data acquisition	$T = 733 / 743 / 753 / 763$ K WHSV(<i>n</i> -C ₁₀) = 60 / 160 / 240 / 340 h ⁻¹ 3 bar absolute H ₂ / <i>n</i> -C ₁₀ = 6 mol/mol	The temperature indicated is the unit regulation temperature 3 analyses / reactor / operating condition 1 h / operating condition

bed height / average particle diameter ratio of 48 and reactor diameter / average particle diameter ratio greater than 10. During each test, a reference catalyst is systematically evaluated in two reactors to ensure that the results are reproducible.

The feedstock consists of *n*-decane (anhydrous, 99%, Aldrich) mixed with 500 ppm of water in the form of *iso*-propanol (99.5%, Aldrich). Catalysts cannot be evaluated at the same temperature by the Spider test unit, but a large number of data for each catalyst can be obtained using the fast GC analysis method. We therefore decided to acquire a sufficient number of data at variable temperatures and contact times for each catalyst in order to calibrate two kinetic models according to two simplified reaction mechanisms. Each catalyst is therefore evaluated under sixteen different sets of operating conditions according to the catalytic test protocol described in Table 3. It generally takes three days to conduct a catalytic test. The simplified kinetic models can then be used to compare the catalysts under the same operating conditions and variable contact times. Section 2 provides a detailed explanation of this kinetic approach. During the first tests, it appeared that the initial stabilisation period was not long enough and that the entire duration of a test was required to stabilise the catalyst, mainly due to elution of a large proportion of the chlorine. Consequently, the catalysts were systematically evaluated on two successive tests on the unit; only data from the second test were used to calibrate the simplified kinetic models.

1.2.4 Catalytic Tests Data Management

All data of a catalytic test (catalyst references, operating conditions, GC analysis results) are stored in a company database. A catalytic test generates a very large number of data, typically 720 chromatograms and associated operating

conditions, hence the need for the experimenter to have data validation aid tools. Business Object software can be used to create monitoring requests to display graphically, for each reactor and depending on the time on stream, the change in setpoint values and sensor data during a GC analysis, and the change in contents of the various families for a GC analysis. Aberrant GC analyses and nonconform operating conditions are then eliminated from the database and only validated data are used to calibrate the kinetic models. The parameters of the calibrated kinetic models and the catalytic descriptors obtained from the kinetic modeling are then also stored in the database.

2 KINETIC APPROACH

As explained above, the temperature of the reactors was not controlled individually. Consequently, the temperature in each reactor was slightly different from the setpoint temperature, but it was measured. To make up for the temperature discrepancies, a simplified kinetic model is used. Its parameters are estimated by minimising the sum of squares of the deviations between predictions of the model and observed values. Predictions are then made with the adjusted model and used to compare the catalysts. The approach is detailed in the following paragraphs.

2.1 Kinetic Mechanisms

The choice of the mechanism was determined by the fact that the fast GC analysis did not provide a detailed analysis of the products. In particular, all the light species were grouped in a single family, making it impossible to distinguish hydrogenolysis products from hydrocracking products as well as isomerisation products. Two kinetic mechanisms were considered, differing in the reaction forming Light Products (LP): in the first one, light products are produced by olefin cracking; in the second one, light products are produced by paraffin cracking (Tab. 4).

nP_{10} stands for *n*-decane, O_{10} for olefins with 10 carbon atoms, diO_{10} for diolefins with 10 carbon atoms, A_{10} for

TABLE 4
Two simplified kinetic mechanisms considered for the study

	First mechanism	Second mechanism
R1	$nP_{10} \rightleftharpoons O_{10} + H_2$	$nP_{10} \rightleftharpoons O_{10} + H_2$
R2	$O_{10} \rightleftharpoons diO_{10} + H_2$	$O_{10} \rightleftharpoons diO_{10} + H_2$
R3	$diO_{10} \rightarrow A_{10} + 2 H_2$	$diO_{10} \rightarrow A_{10} + 2 H_2$
R4	$O_{10} + H_2 \rightarrow 2 LP$	$nP_{10} + H_2 \rightarrow 2 LP$

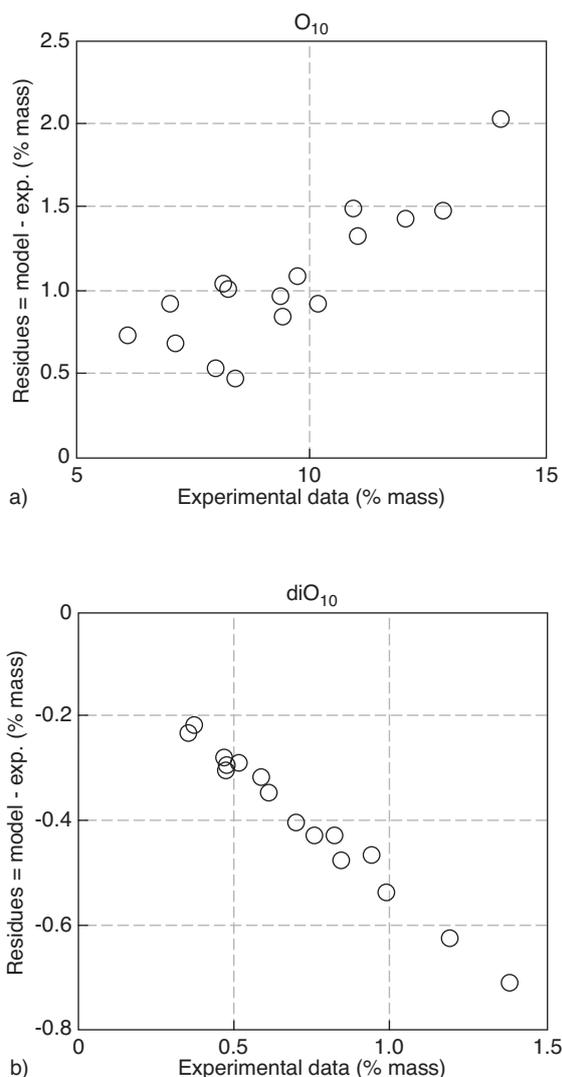


Figure 4

An example of residues when the equilibrium constants are calculated with the Benson correlation: olefins a), diolefins b) (the experimental results were obtained in reactor 1 with a reference catalyst).

aromatics with 10 carbon atoms. The dehydrogenation reactions forming olefins and diolefins are reversible. The other two reactions are irreversible.

2.2 Reaction Rates

In the catalytic tests, only contact time and temperature were varied. The reactants were *n*-decane and hydrogen in a fixed proportion. The pressure was also held constant. A simple form for the reaction rates was chosen, so as to limit the number of unknown parameters to be estimated: all the reaction

rates are first order in reactant partial pressure (the reaction takes place in a gas phase). For example, the reaction rate of the first reaction is:

$$r_1 = k_1^0 \exp\left(-\frac{E_{a,1}}{RT}\right) \left(P_{n\text{P}10} - \frac{P_{\text{O}10}P_{\text{H}_2}}{K_1(T)}\right)$$

In this expression, k_1^0 is the pre-exponential factor, $E_{a,1}$ is the activation energy, R is the gas constant, T is the temperature, P_i is the partial pressure of species i and $K_1(T)$ is the equilibrium constant of the reaction.

Eight parameters must be estimated: the four pre-exponential factors and the four activation energies. The equilibrium constant is assumed to be known.

2.3 Reactor Model

The reactor is assumed to be ideal: plug-flow, no mass transfer limitations. The gas-phase is also assumed to be ideal. Only the steady state is considered. The model is a system of differential equations, each equation representing a mass-balance for one species.

2.4 Equilibrium Constants

At first, the Benson correlation was used to calculate the equilibrium constants of reactions R1 and R2. A series of catalytic tests was performed with a reference catalyst in the 16 reactors: in each reactor, time on stream and temperature were varied on a grid, each taking 4 different values.

The eight kinetic parameters of the second mechanism were then estimated (similar results were obtained with the first mechanism), resulting in 16 sets of parameters, one for each reactor. A residue diagram for olefins and diolefins in reactor 1 is shown in Figure 4: the abscissas are the mass percentage of olefins and diolefins in the products, the ordinates are the differences between the model predictions and the experimental values. It can be seen that olefins are over-estimated and that diolefins are underestimated. Similar results were obtained in the other 15 reactors.

To reduce this bias, each equilibrium constant was multiplied by a factor to be estimated. These two factors were added to the kinetic parameters and new estimations were made with the second mechanism (the estimation was also made with the first mechanism, but the predictions were not as good as with the second mechanism). A set of 10 parameters (8 kinetic parameters plus 2 multiplicative factors) was obtained for each of the 16 reactors. The multiplicative factors are shown in Figure 5 for each reactor.

The values of the first multiplicative factor can be grouped into 2 subsets: one for reactors 1-8, another for reactors 9-16. This is due to the differences in the GC-analysis as explained above. Nothing similar can be noticed for the second multiplicative factor. The multiplicative factors were then averaged and set to the mean values (see Tab. 5).

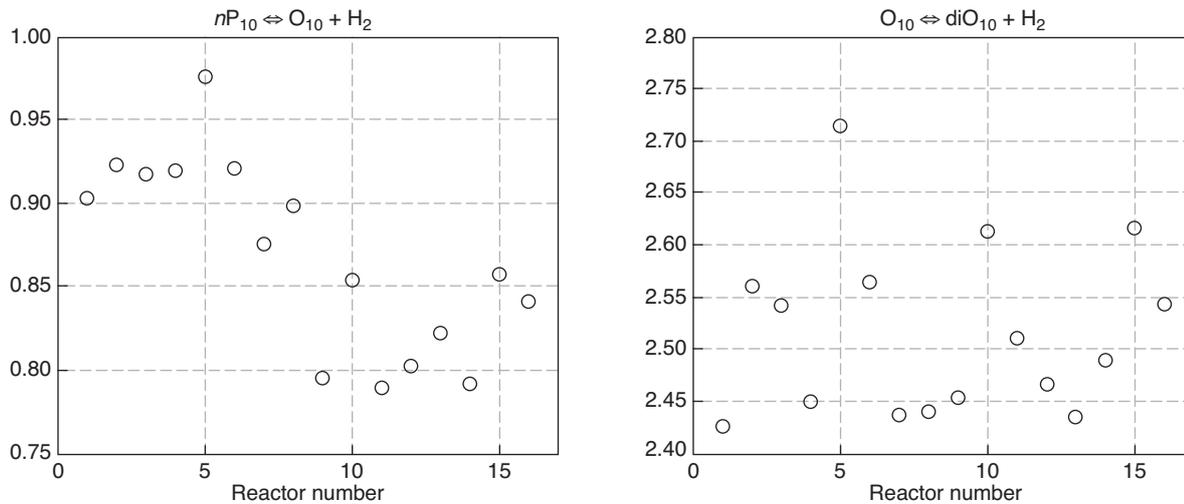


Figure 5

Multiplicative factors of the equilibrium constants of the reversible reactions.

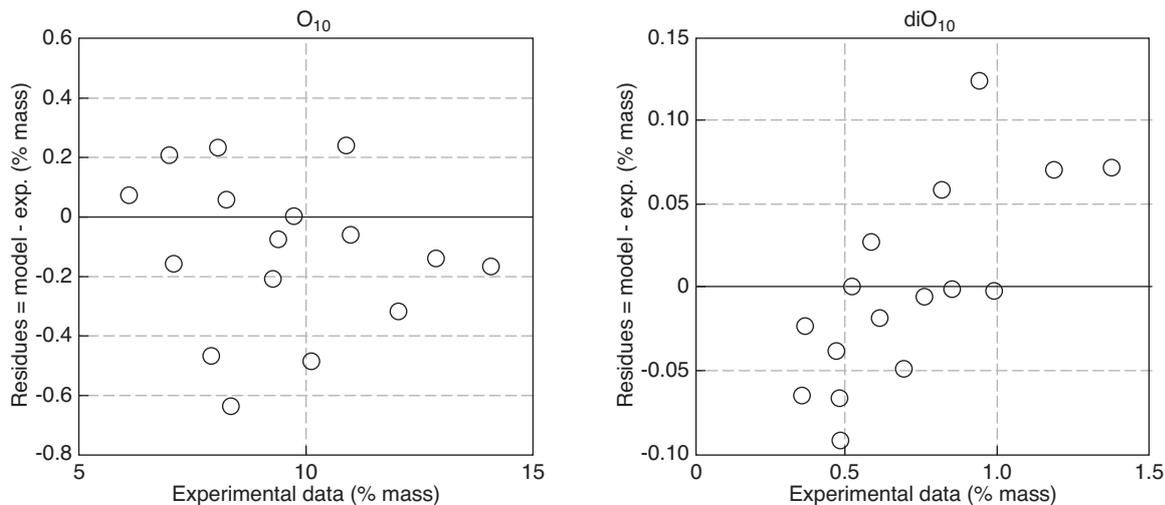


Figure 6

Residue diagram after modification of the equilibrium constants (equivalent of Fig. 5).

TABLE 5

Mean values of the multiplicative factors of the equilibrium constants

$nP_{10} \rightleftharpoons O_{10} + H_2$	0.87
$O_{10} \rightleftharpoons diO_{10} + H_2$	2.5

A new estimation of the eight kinetic parameters of the second mechanism was made with the modified values of the equilibrium constants. The results for reactor 1 are shown in Figure 6. The bias has been almost completely removed. Similar results are obtained with the other reactors.

2.5 Summary of the Kinetic Approach

For each catalyst, a series of catalytic tests is made in one reactor. In these tests, time on stream and temperature are varied on a grid, each variable taking 4 different values. The eight parameters of both kinetic mechanisms are then estimated (the equilibrium constants are the Benson values multiplied by the factors of Tab. 5, as explained above). The best mechanism (*i.e.* the one with the lowest sum of squares of deviations) is chosen to compute predictions for a reference conversion of *n*-decane (8%) at a reference temperature

(743 K), total pressure (300 kPa) and hydrogen to *n*-decane molar ratio (6 mol/mol).

The following catalytic descriptors are used for the catalyst ranking:

- relative catalyst activity, defined as follows:

$$A(\text{catalyst}) = \text{WHSV}(\text{catalyst}) / \text{WHSV}(\text{reference}) \times 100$$
 where $\text{WHSV}(\text{catalyst})$ is the WHSV required to reach 8% conversion for a given catalyst and $\text{WHSV}(\text{reference})$ is the WHSV required to reach 8% conversion for the reference catalyst;
- C₁₀ olefins yield at 8% *n*-decane conversion;
- C₁₀ diolefins yield at 8% *n*-decane conversion;
- aromatics yield at 8% *n*-decane conversion;
- cracking and isomerisation products yield at 8% *n*-decane conversion.

3 CATALYST FORMULATION OPTIMISATION

3.1 Study Domain — Factors and Responses — Design of Experiments

The domain chosen to optimise a trimetallic “Pt-Sn-X” catalyst formulation is bounded by the following contents for each element:

- Pt: 0.1 to 0.4% by weight;
- Sn: 0.1 to 0.5% by weight;
- X: 0 to 0.4% by weight.

The content of each element is independent of the content of the other two.

Catalyst performance is calculated using a kinetic model according to the approach described in Section 2.

The advantage of using design of experiments in this study is the ability to construct, from a limited number of experiments, a mathematical model of prediction variance as low as possible, associating each response with the three factors. Once the mathematical model has been built and validated, it will be used to find a catalyst offering optimum characteristics with respect to the responses studied.

The approach adopted is known as Response Surface Methodology (RSM) [12, 13] due to the fact that the mathematical model, after being built and validated, is valid throughout the specified experimental domain (any extrapolation outside this domain would be incorrect).

To approximate each response using the 3 factors of the study, we choose a polynomial model of degree 2. The design of experiments method then consists in defining the experiments to be conducted, which should be as few as possible, in order to estimate the coefficients of such models. These experiments taken together represent a design of experiments. To build these designs, the experimenter is faced

with a certain number of methods which differ as regards the mathematical criteria involved, mathematical properties (orthogonality, variance of the model built, etc.) and the number of experiments (experimental cost) which varies from one method to another, in the designs resulting from these methods. These methods, each with their own advantages and disadvantages, should be adapted according to the problems posed, the study context and the number of factors in the study.

In this study, we decided to adopt a D-optimality approach to build the design of experiments. Based on an iterative algorithm, this technique consists in selecting, amongst the various possible experiments – known as candidates – in the experimental domain, a set of experiments that will minimise the determinant of the information matrix. For further details on this technique, refer for example to Myers and Montgomery [14]. The advantage of D-optimality lies in its flexibility regarding the user’s choice of candidate points. They are generally formed by a regular meshing of the experimental domain. We preferred this method to more traditional approaches, such as central composite designs [14], which offer little freedom regarding the choice and location of the experiments to be conducted.

3.2 Catalytic Tests Results

The design obtained by D-optimality — called the D-optimal design — is shown in Table 6. Each line in the table corresponds to the formulation of a catalyst. Lines numbers from 1 to 16 and 22 to 28 correspond to catalysts with different formulations. Lines numbered 17 to 21 correspond to different catalysts with the same theoretical formulation located in the centre of the experimental domain. The results obtained on catalysts 17 to 21 can therefore be used to evaluate the experimental variance at the centre of the domain associated with the preparation and evaluation of catalysts with our high throughput experimentation tools. The last 7 catalysts (numbers 22 to 28) are not used to build the model, but to evaluate its prediction quality. They therefore act as model validation points.

A polynomial model has been built for each response, using the results of the first 16 catalysts and the 5 points at the centre.

3.2.1 Consistency Between Kinetic Modeling and Experimental Results

Before using the kinetic modeling results, we checked that the experimental results and those obtained from the kinetic modeling were consistent. Satisfactory results were obtained for all catalysts, in agreement with the low values of the sum of squares of the deviations. For example, the parity diagrams obtained for catalyst 28, whose kinetic modeling is the least efficient, are shown in Figure 7.

TABLE 6
Target formulations of the catalysts prepared and evaluated
in catalytic test (D-Optimal design)

Number	wt% Pt	wt% Sn	wt% X
1	0.1	0.1	0
2	0.4	0.1	0
3	0.1	0.3	0
4	0.3	0.3	0
5	0.1	0.5	0
6	0.4	0.5	0
7	0.4	0.5	0.11
8	0.2	0.1	0.24
9	0.4	0.3	0.24
10	0.1	0.5	0.24
11	0.1	0.1	0.37
12	0.4	0.1	0.37
13	0.1	0.3	0.37
14	0.1	0.5	0.37
15	0.3	0.5	0.37
16	0.4	0.5	0.37
17	0.25	0.3	0.24
18	0.25	0.3	0.24
19	0.25	0.3	0.24
20	0.25	0.3	0.24
21	0.25	0.3	0.24
22	0.17	0.25	0.24
23	0.31	0.25	0.24
24	0.25	0.4	0.24
25	0.25	0.3	0.24
26	0.17	0.25	0.24
27	0.25	0.2	0.24
28	0.31	0.4	0.24

3.2.2 Correlation Between Catalyst Product Yields and Relative Activities

Before building response surfaces in order to correlate catalytic properties and catalyst composition, we examined the results obtained with all the catalysts in the design of experiments without taking their composition into account; we observed that the activity and product yields are not independent. Figure 8 represents the change in product yields as a function of the relative activity for all catalysts of the design. An increase in the catalyst relative activity induces a decrease in the yields of aromatics and cracking/isomerisation products

with a corresponding increase in the production of olefins and even diolefins. It is as though the increase in activity of the catalyst favoured its selectivity towards the dehydrogenation reaction.

The change in conversion and product yields as a function of the contact time as predicted by the model for catalysts 16 (the most active in the domain, relative activity 352), 17 (intermediate activity, relative activity 235) and 1 (the least active in the domain, relative activity 116) explains the origin of the phenomenon (Fig. 9). We observe that logically catalyst 16, the most active, exhibits the highest conversion at equal contact time in the kinetic domain. The change in product yields as a function of contact time shows that the activity variations for these three catalysts are specifically due to variations in the dehydrogenating activities of the solids (production of olefins and diolefins) while the rates of formation of the other products are virtually identical. Within our study domain, the highest selectivity of the most active catalysts could therefore be accounted for by a specific increase in the dehydrogenating activity of the catalyst, at equal activity in cracking, isomerisation and aromatisation. The virtually identical activity of the three catalysts for the production of cracking/isomerisation products and aromatics is worth mentioning. From the mechanistic point of view, it is known that dehydrogenation is a monofunctional metallic reaction, but that the cracking, isomerisation and aromatisation reactions may be bifunctional with a role played by the Bronsted acidity of the support (see Fig. 1). In our study domain, the support used and the initial level of residual chlorine are the same for all catalysts (see Sect. 1.1.3). If we assume that the residual acidity of the catalyst is only slightly affected by the quantity of metals introduced on the support, the catalysts of the design exhibit comparable Bronsted acidity. We might also consider that for the formation of products involving bifunctional mechanisms, the acid function is limiting (acid function: alumina support with low chlorine content; hydro/dehydrogenating function of noble metal type). The result is that the cracking/isomerisation and aromatisation activity must in fact be very similar for all the catalysts and independent from the metallic function. Conceptually, we can say that at the same residual acidity and assuming that the formation of coproducts mainly involves bifunctional mechanisms, maximising the selectivity of a catalyst goes hand in hand with maximising the activity of the dehydrogenating function.

3.2.3 Variability of the Design of Experiments Responses and Experimental Variance

Before building polynomial models aimed at predicting catalytic performance from the catalyst composition, we first checked whether the “quality” of the information to be modelled is good enough to build the models. The “quality” of this information can be evaluated by comparing the experimental variance of the design responses and the repeatability variance evaluated using the repeated point at the centre of

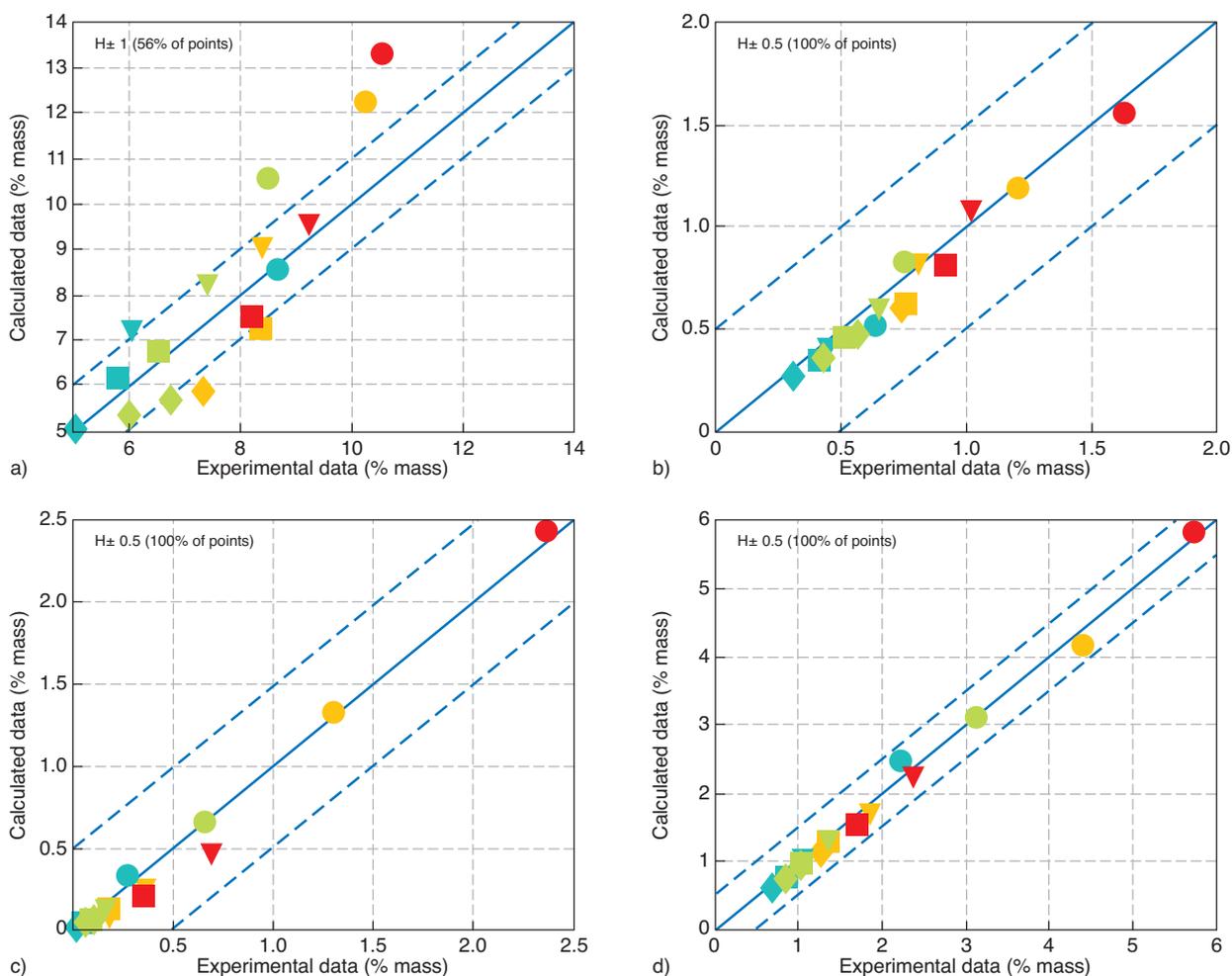


Figure 7

Parity diagrams for yields in a) olefins, b) diolefins, c) aromatics and d) cracking and isomerisation products for catalyst 28 of the design of experiments.

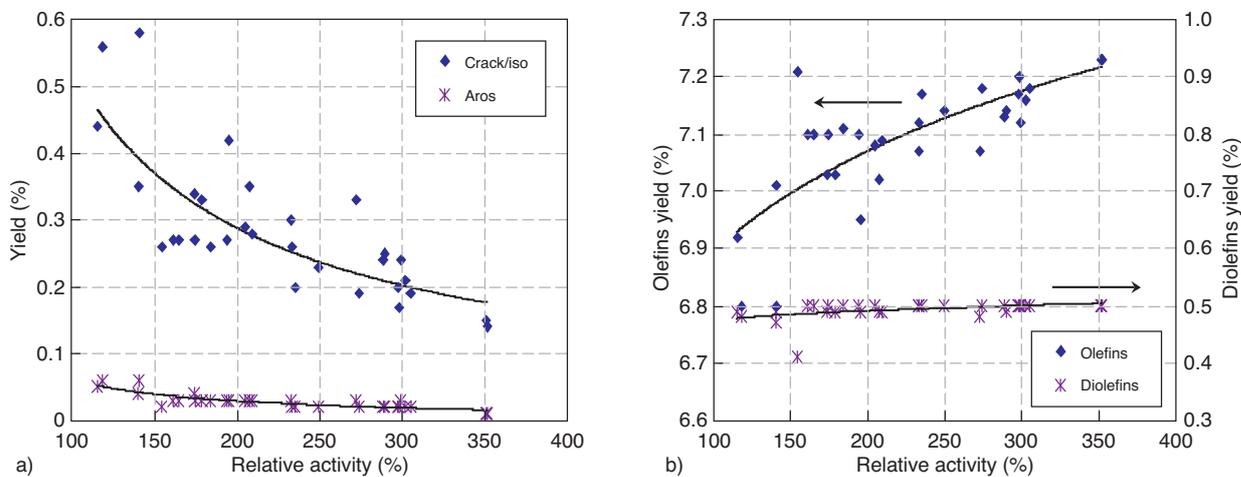


Figure 8

Change in yields in a) aromatics and cracking and isomerisation products and b) olefins and diolefins as a function of the relative activity (predicted values at 8% conversion) for all catalysts tested.

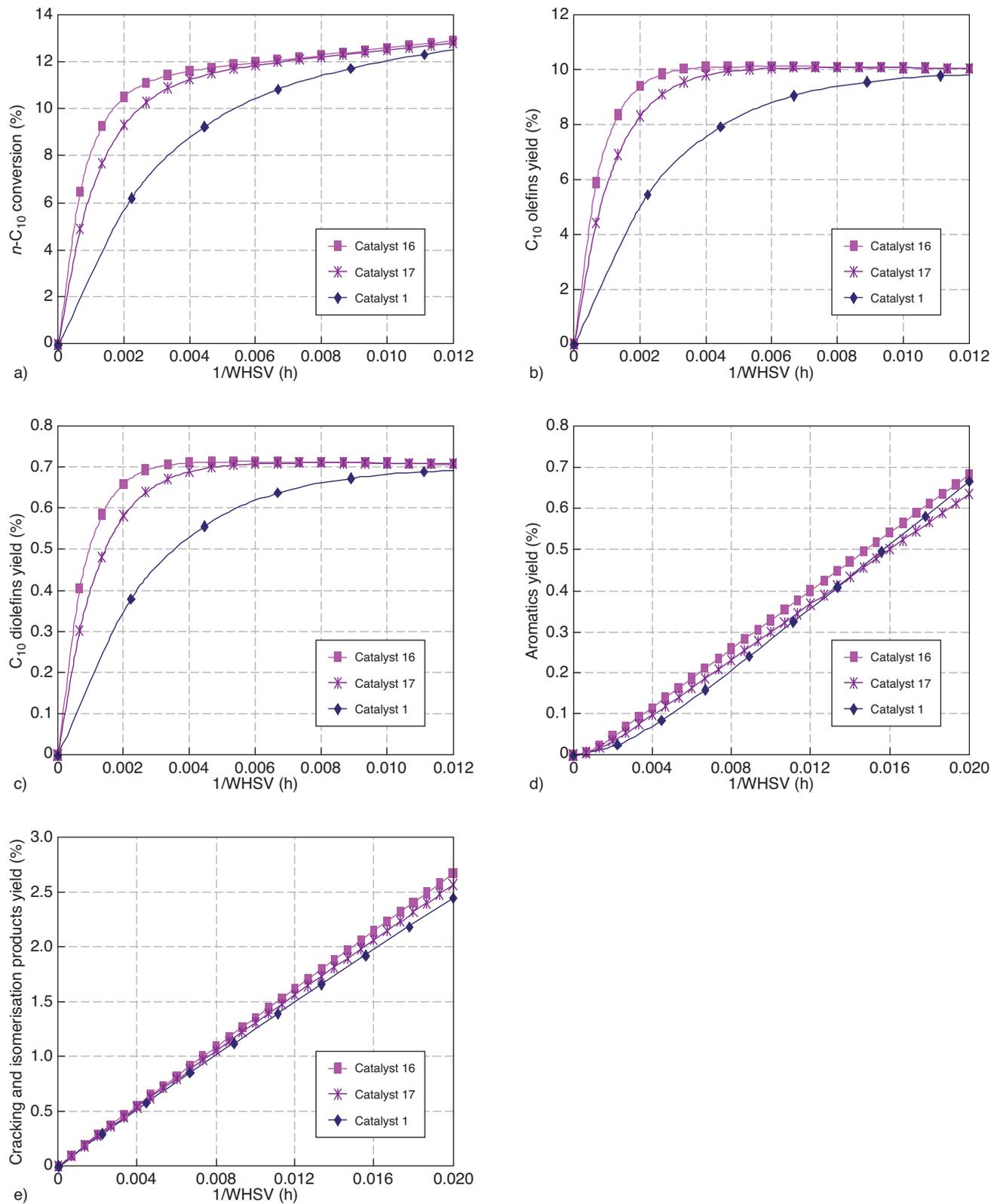


Figure 9

Change in a) conversion of n -decane and yields in b) olefins, c) diolefins, d) aromatics and e) cracking/isomerisation products as a function of the contact time predicted by the kinetic model for catalysts 1, 16 and 17.

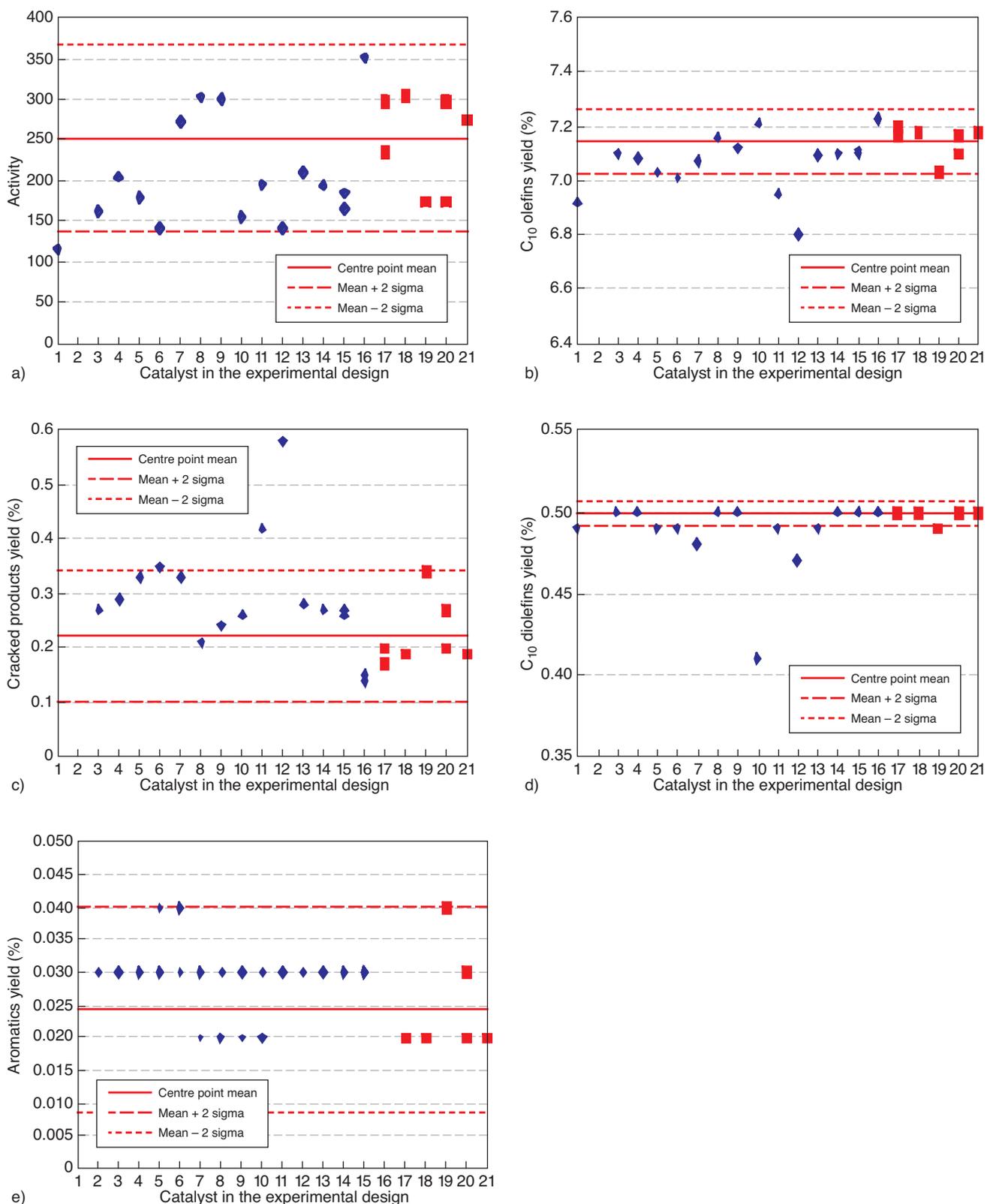


Figure 10

Positioning of a) the relative activity and yields in b) olefins, c) cracked products, d) diolefins and e) aromatics predicted by the kinetic model for the catalysts of the D-optimal design compared with the respective mean values ± 2 standard deviations calculated from the repetition of the centre point.

the domain (experimental noise). For each response to be modelled, Figure 10 shows the values obtained for the various catalysts in the design, which are compared with the mean value of the repetitions of the central point \pm twice the repeatability standard deviation (95% confidence interval). The order in which the points are represented on the horizontal axis corresponds to the numbering of the catalysts in Table 6. Depending on the responses considered, only one to three catalysts of the design lie outside the 95% confidence interval; given the insufficient “quality” of the data set, it appears incongruous to consider any modeling of catalytic performance as a function of the catalyst composition in the study domain chosen. These results demonstrate that for this study, with the chosen experimental domain and the experimental tools available, it is impossible to model a catalyst composition since the variation of the catalytic properties depending on the catalytic formulations of the design of experiments is not large enough with respect to the experimental variance.

Consequently, the initial objective of the study, to optimise the formation of trimetallic “Pt-Sn-X” model catalysts, has not been achieved. Note, however, that this result could not have been obtained and confirmed without the use of design of experiments. As we have just seen, the required model explaining catalytic performance as a function of the catalyst composition could not be estimated due to the high experimental variability. To build this model, however, we had to conduct suitable experiments in the experimental domain which have led to this result. This conclusion is not specifically a direct consequence of the design of experiments, but of the resulting experiment planning.

3.2.4. Conclusions

To optimise a trimetallic “Pt-Sn-X” model dehydrogenation catalyst formulation on an alumina support within a defined study space, an approach based on use of a design of experiments to build a mathematical prediction model (polynomial model of degree 2) has been implemented.

Analysis of the results obtained for all catalysts in the design of experiments has confirmed a key concept for maximising the selectivity of a catalyst. At the same residual acidity and assuming that the formation of coproducts mainly involves bifunctional mechanisms, maximising the selectivity of a catalyst goes hand in hand with maximising the activity of its dehydrogenating function.

In contrast, with the chosen study domain and the experimental tools available, catalyst composition cannot be optimised by building a mathematical model since the variation of the responses depending on the catalytic formulations of the design of experiments is not large enough with respect to the experimental variance.

CONCLUSIONS

Use of high throughput experimentation tools may be interesting to optimise catalysts with multimetallic formulations, firstly due to the increasing number of possible formulations with the number of elements considered and secondly due to the possible existence of nonlinear interactions between the elements. Catalysts used for dehydrogenation of long chain paraffins generally involve multimetallic formulations.

This article is therefore dedicated to a description of the high throughput experimentation tools used for preparation and catalytic evaluation during dehydrogenation of *n*-decane of alumina-supported “Pt-Sn-X” model catalysts, to the strategy used to optimise the formulation and to the experimental results obtained.

In view of the thermodynamic limitations inherent to the dehydrogenation reaction and the technical limitations of the catalytic test tool, a specific test protocol had to be developed as well as a simplified kinetic model to compare catalysts at the same conversion of *n*-decane and the same operating conditions (apart from the contact time).

An approach based on the use of design of experiments to build a mathematical prediction model has been implemented to attempt to optimise the formulation of trimetallic “Pt-Sn-X” catalysts within a defined study domain. This approach could not be completed since the variation of the responses depending on the catalytic formulations of the design of experiments is not large enough with respect to the experimental variance.

Analysis of the results obtained for all catalysts nevertheless confirmed a key concept for maximising the selectivity of a long chain paraffin dehydrogenation catalyst. At the same residual acidity and assuming that the formation of coproducts mainly involves bifunctional mechanisms for which the limiting step occurs on the acid phase, maximising the selectivity goes hand in hand with maximising the activity of the catalytic dehydrogenating function.

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