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Holographic research strategy for catalyst library design Description of a new powerful optimisation method

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Abstract

The principle of a deterministic optimisation algorithm called holographic research strategy (HRS) has been described. It has been demonstrated that in a multidimensional experimental space having around 63 000 potential experimental points less than 200 virtual experiments were sufficient to find the global maximum. The benefits of the use of HRS are as follows: (i) easy application to catalyst library design, (ii) fast method in finding the global optimum, and (iii) good visualisation of a multidimensional experimental space.

Keywords: Combinatorial catalysis; Catalyst library design; Optimisation algorithm

1. Introduction

Combinatorial approach and high throughput experimentation (HTE) techniques enable rapid screening of broad experimental parameter space characteristic for heterogeneous catalysis. In the process of discovery of new catalytic materials the advantage of HTE approaches over traditional ones has already been demonstrated by different research groups [1–3].

Traditional methods of catalyst development are based on rational approaches, i.e., use of literature data, previous scientific knowledge and methods of design of experiments (DOEs). Full or fractional factorial designs are frequently used in catalyst development to optimise catalyst performance [4]. A relatively good description of catalytic properties in a multidimensional parameter space can be achieved by using methods of DOE [5], however, the number of experiments to be done is relatively large.

In HTE, despite the parallel catalyst screening, due to the (i) large number of binary, ternary or quaternary combinations of possible catalytic elements, (ii) variety of preparation parameters, a huge number of experiments should be performed. To overcome this problem different search algorithms have been developed, such as (i) the genetic algorithm (GA) [6], and (ii) the stochastic simulated annealing algorithm [7]. These algorithms are able to find the optimal catalyst composition or reaction parameter values by performing only a minor part of the possible number of experiments.

We describe here a new strategy, i.e., holographic research strategy (HRS) for the design and testing of catalyst libraries. This approach has been used in this study for virtual preparation and testing of relatively large number of multi-component catalysts. In the HRS similarly to other methods, such as the GA,

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test results of the $(n-1)$th generation is used to design the nth generation. Consequently, the new approach is considered as an iterative process. However, as it will be shown the new strategy appears to be a deterministic one. From this point of view it resembles methods of factorial DOE, but contrary to that HRS provides always the global maximum.

In combinatorial approaches the designed catalysts are prepared and tested parallel using methods of HTE. After testing the catalysts are ranked. This rank is usually called "elite list" which is used to design the next catalyst generation. In this study multi-component heterogeneous catalysts have been virtually "prepared and tested" by means of an arbitrary objective function.

2. Experimental

A hypothetical multi-component supported metal catalyst library has been designed and virtually tested using the newly developed HRS. The number of metal components (N) was eight and each component has been adjusted in the 0–5% range having 4–5 concentration levels according to Table 1. Catalysts were created in such a way that the total metal content should not beyond 6%. Accordingly, the total number of combinations of all possible catalyst compositions is 63 528.

The oxidation of CO over hypothetical Pt and Pd based multi-component catalysts has been chosen as a virtual reaction. The objective function (1) has been used to describe the yield of CO_2 (Y_{CO_2}) as a function of metal content (given in wt.%, see Table 1).

$$\begin{aligned} Y_{CO_2} = {} & 4.5\mathrm{Pt} + 0.5\mathrm{Pd} + 0.5\mathrm{Ru} + 0.5\mathrm{PtPd}(\mathrm{Pt}+1) \\ & \times (\mathrm{Pd}+0.1) + \mathrm{PtSn}(\mathrm{Pt}-0.8)(\mathrm{Sn}+0.8) \\ & + \mathrm{PtPdSn}(\mathrm{Pt}+\mathrm{Pd})(\mathrm{Sn}+1) + \mathrm{RuSn}(\mathrm{Sn}+1) \\ & \times (\mathrm{Ru}-0.1) - 0.1(\mathrm{Ge}+\mathrm{In})(\mathrm{Pt}+\mathrm{Pd}+\mathrm{Ru}) \end{aligned} \quad (1)$$

Table 1
Concentration levels of the components of catalysts

Levels	Components (wt.%)							
	Pt	Pb	Sn	In	Ga	Ge	Ru	Pd
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	0.6	0.3	0.6	0.4	0.3	0.4	0.2	0.5
3	1.2	0.6	1.1	0.8	0.6	0.8	0.4	1.0
4	1.7	0.8	1.5	1.1	0.8	1.1	0.5	1.4
5	2.1	–	–	–	–	–	–	–

In a recent study [6] a similar approach, i.e., the use of an objective function describing the yield as a function of catalyst composition has been applied to demonstrate the development of "an evolutionary approach in the combinatorial selection and optimisation of catalytic materials".

All the computations have been done using LINUX environment and a *personal computer*. The HRS has been included into a software package (*Xhrs for Linux*) written for PCs. The *Xhrs for Linux* contains the code for the algorithm described here and provides user-friendly interfaces. It is connected to data-acquisition and process control software (*Xmea for Linux*). Both softwares have been developed by the Meditor General Innovation Bureau.

3. Results and discussion

3.1. The principle of holographic research strategy (HRS)

The principle of HRS is based on a special, two-dimensional presentation of a continuous multi-dimensional experimental space. As a primary assumption it has been accepted that most of the cases the experimental space related to catalyst library design is continuous. As a consequence, two proximate experimental points in the given multidimensional space should have very similar property. Due to the special two-dimensional transformation applied in this approach the continuity of the multidimensional experimental space is maintained.

Let us demonstrate the continuity in the presentation of hypothetical experimental variables A and B. Let us assume that these two variables have three parameter levels, A_1, A_2, A_3 ($A_1 < A_2 < A_3$) and B_1, B_2, B_3 ($B_1 < B_2 < B_3$), respectively. For these two variables different experimental designs can be applied as shown in Table 2a and b. The nine experiments arranged in Table 2a show a definite discontinuity, as there is a sudden drop in the level of variable B after it has reached its highest level. Contrary to that the arrangement given in Table 2b is continuous, as the level of variable B increases gradually till it reaches its maximum then it decreases gradually again. The main consequence is that in

Table 2
Experimental design

	Experiments								
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th
(a) Traditional order of realisation									
Levels of variable, *A*	A_1	A_1	A_1	A_2	A_2	A_2	A_3	A_3	A_3
Levels of variable, *B*	B_1	B_2	B_3	B_1	B_2	B_3	B_1	B_2	B_3
(b) Proposed order of realisation									
Levels of variable, *A*	A_1	A_1	A_1	A_2	A_2	A_2	A_3	A_3	A_3
Levels of variable, *B*	B_1	B_2	B_3	B_3	B_2	B_1	B_1	B_2	B_3

experimental design shown in Table 2b two consecutive experimental points differ from each other only in one parameter level of one of the experimental variables.

Increasing the number of variables and/or their levels the size of the experimental space increases drastically. For this reason the visualisation of a continuous multidimensional experimental space requires a special, two-dimensional presentation of experimental points. Fig. 1 shows the presentation of a six dimensional experimental space in two dimensions. It has to be emphasised that this example does not refer to our case study but is only a mean to show how the HRS works. Characteristic feature of this mode of presentation is as follows:

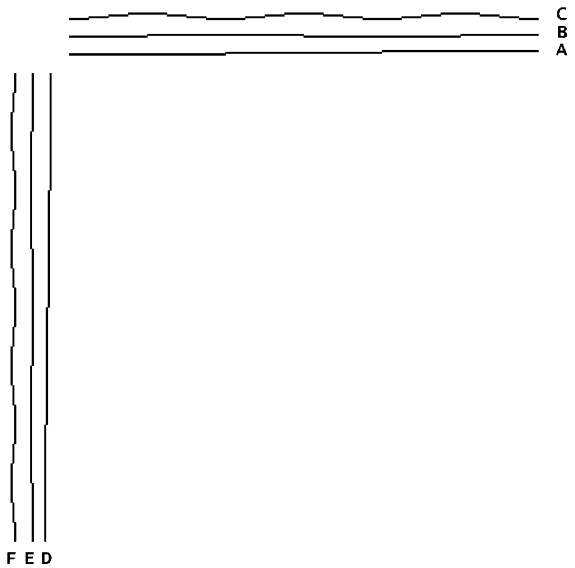

Fig. 1. Two-dimensional presentation of a continuous six-dimensional experimental space.

- Three experimental variables are placed optionally along the *X*-axis and three along the *Y*-axis (the experimental variables are designated by different capital letters and their increasing or decreasing parameter levels are represented by lines forming full or partial waves as shown in Fig. 1);
- The levels of experimental variables are arranged in such a way that each component has different periodicity;
- The level of each variable increases gradually till it reaches its maximum. Depending on the periodicity the level of given variable decreases faster or slower.

Accordingly, moving along any axis from one experimental point to the next one only one level of one variable is changed. Due to the last feature the two-dimensional transformation of the experimental space is continuous, consequently there are only small differences in the neighbourhood of each experimental point. This kind of presentation should result in continuous changes in the properties of catalysts with composition. This general mode of visualisation of the multidimensional experimental space has been mentioned first by Tejfalussy [8].

Experimental data generated by a hypothetical function with six variables were arranged as shown in Fig. 2a. Hypothetical experimental data are shown by different shades of grey. The closer the data to the optimum the darker the colour of the given point. This mode of presentation of experimental points provides a good visualisation of the whole experimental space. This presentation resembles the properties of

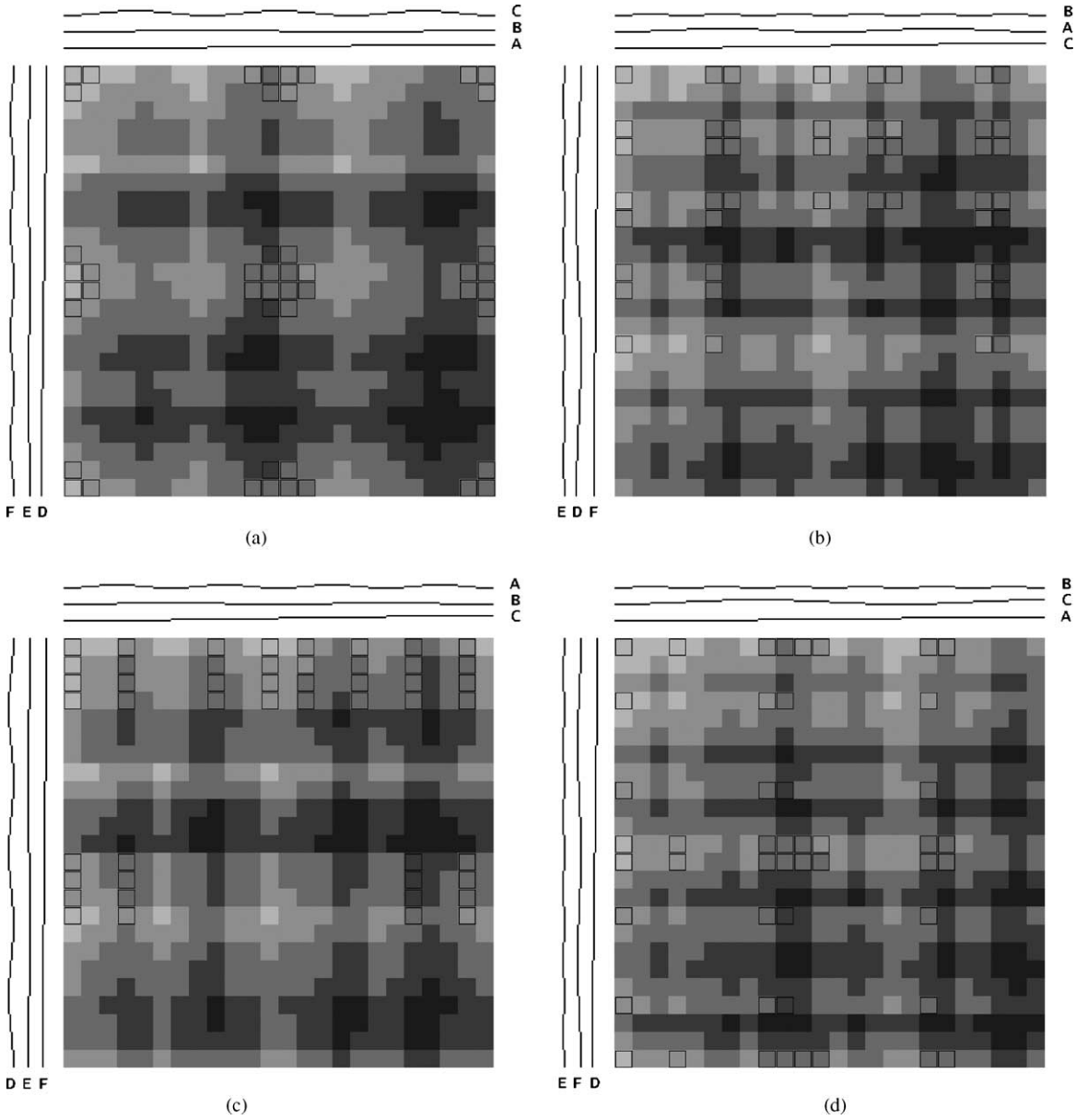

Fig. 2. Influence of "variable position changes" on the holograms.

a hologram. The similarity of our approach with the holography can be summarised as follows:

(i) the two-dimensional presentation used in HRS provides information about the whole experimental space;

(ii) the two-dimensional presentation can be considered as a continuous transformation of the multi-dimensional experimental space.

It has to be emphasised that in the experimental hologram (see Fig. 2a) there are only small differences

in the neighbourhood of each experimental point. Fig. 2a illustrates only one possible presentation of the experimental space. As it is shown in Fig. 2b–d if the position of experimental variables around *X*- and *Y*-axes is altered the neighbourhood of experimental points is also changed. The change of the position of experimental variables along *X*- and *Y*-axes is called "variable position change". This procedure results in different presentations of the hologram as it is shown in Fig. 2b–d. Due to variable position change each experimental point shall have a new neighbourhood (see the arrangement of the black framed squares in these four figures). The comparison of Fig. 2a and b clearly shows that the initial clusters of experimental points are broken. This phenomenon is called "declusterisation". As a conclusion Fig. 2a–d demonstrate that different order of variables along *X*- and *Y*-axes leads to different arrangement of the experimental points in the hologram.

It should be emphasised that from the point of view of the information content each two-dimensional hologram is equivalent to each other. In other words all hologram contains identical experimental points of the given experimental space. Moreover, each two-dimensional hologram can be considered as a continuous transformation of the experimental space. Fig. 2a–d clearly show that in the neighbourhood of any experimental point only slightly different points can be found. These transformations, i.e., the changing of the order of variables in the hologram, have an essential role in the HRS.

In HRS three approaches can be applied to create the first catalyst generation: (i) application of accumulated knowledge about the reaction and the catalysts used, (ii) creating compositions based on symmetry elements of the hologram, and (iii) using compositions chosen randomly. In this study the symmetry elements were used. Namely, the initial experimental points have been fixed as small clusters (i) in the centre, (ii) along the symmetry axes, and (iii) in the corners (see black framed squares in Fig. 3a). Fig. 3b shows the initial hypothetical catalyst library after its testing.

The further steps in the HRS are shown in Fig. 4a–d. In these figures for sake of easier explanation, the hypothetical experimental data are shown by different colours. Nevertheless, similarly to our previous routine the closer the data to the optimum the darker the colour of the given point. Instead of capital letters the variables are designated by different colours as well.

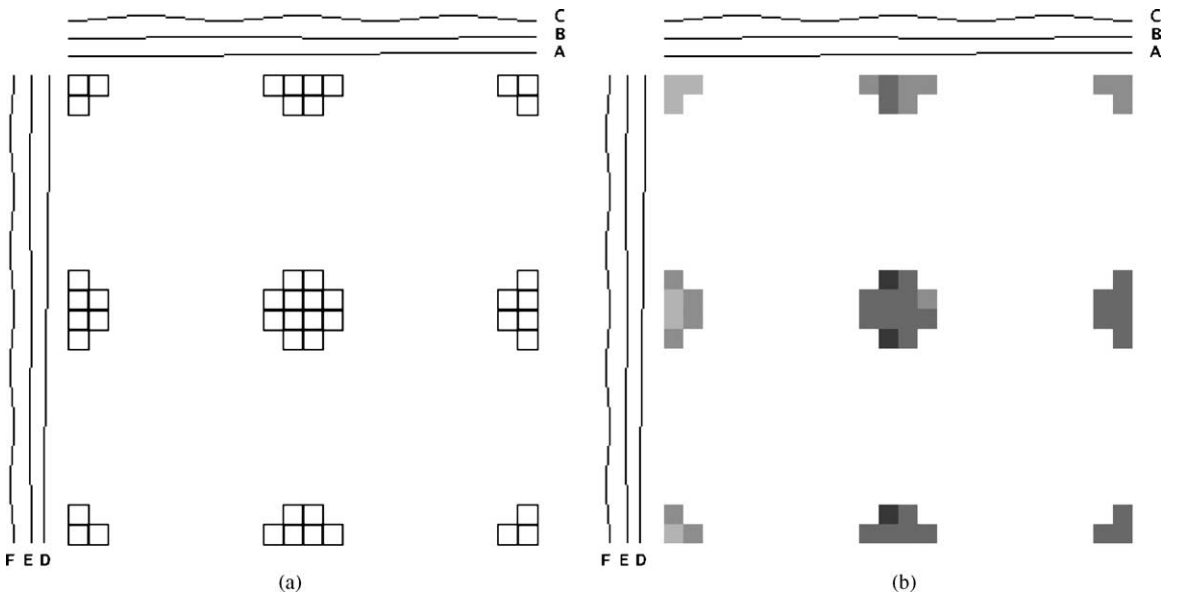

Fig. 3. Formation and testing of the initial hypothetical catalyst library. (a) Catalysts with different composition are selected along the symmetry elements; (b) the initial catalyst library after testing.

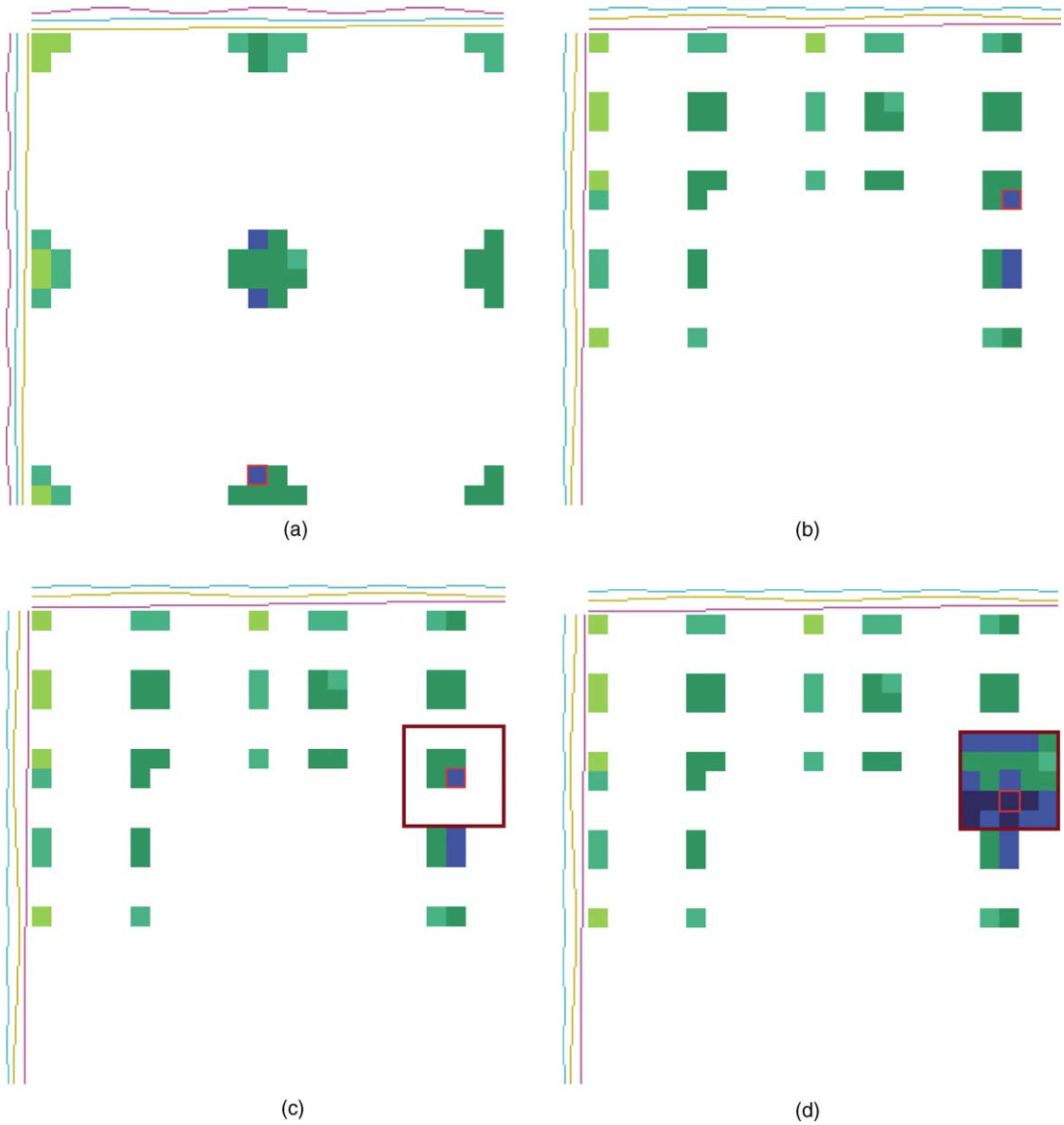

Fig. 4. The main steps in HRS. (a) Selection of the best experimental point; (b) catalyst library after "variable position changes"; (c) formation of an experimental region (brown square in size 5×5); (d) summary of results after testing the second catalyst generation (the brown square represents the second generation).

The iteration is started by the selection of the best experimental point. In Fig. 4a it is highlighted by the small red square. After variable position change the data points of the initial library are arranged as shown in Fig. 4b. In order to create the next catalyst generation an experimental region of size 5×5 is selected around the best experimental point (hit) as shown by the large brown square in Fig. 4c. The results of testing of the second generation are shown in Fig. 4d and the resulted new hit is shown by a small red square.

In the formation of new generation of catalysts the above steps are repeated. Thus, the main steps in

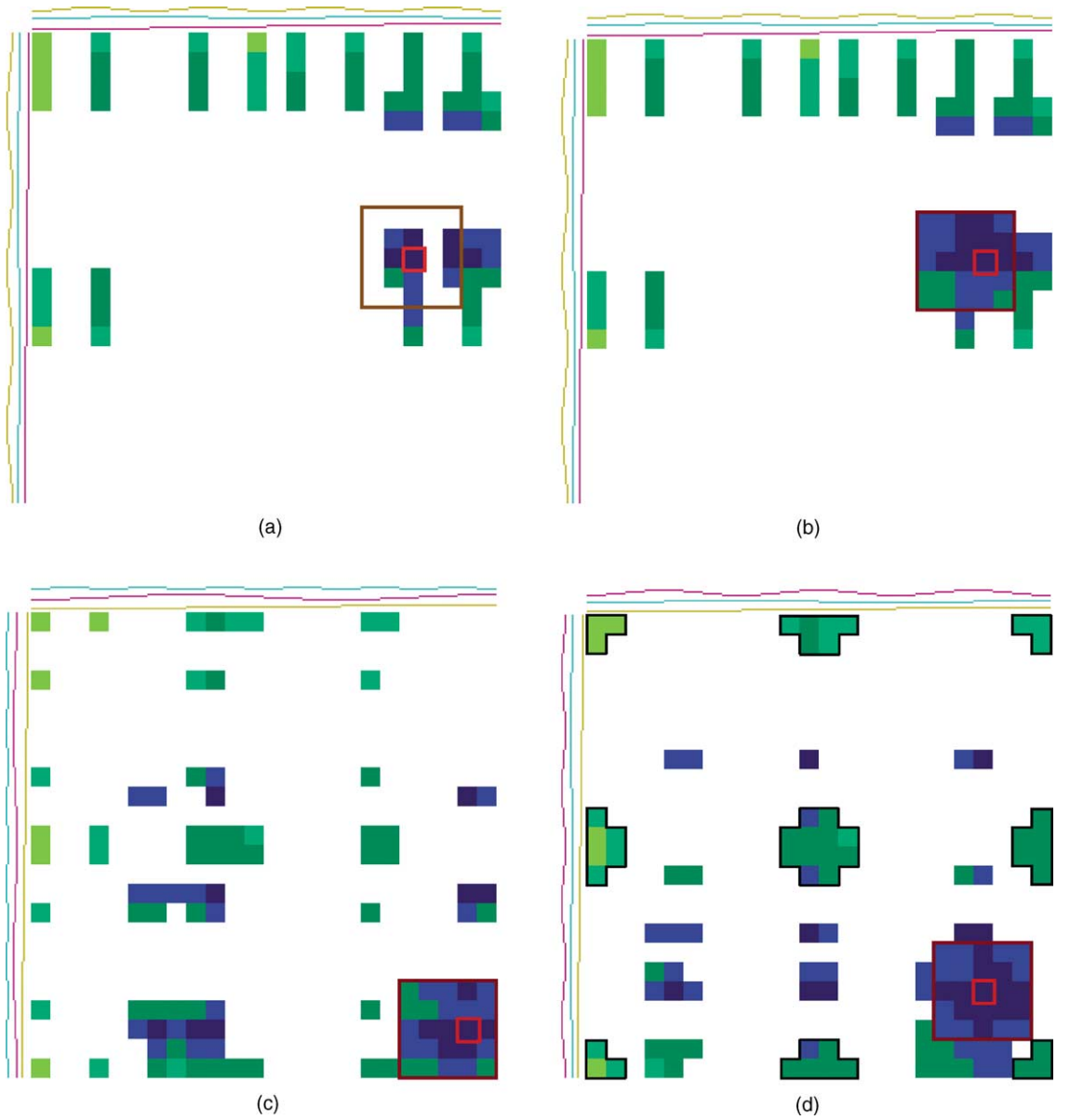

Fig. 5. Iterations, repeating the main steps of HRS. (a) Summary of results after testing the second catalyst generation followed by "variable position change" and formation of the new experimental region (brown square in size 5×5); (b) summary of results after testing the third catalyst generation (the brown square represents the third generation); (c) summary of results after testing the fourth catalyst generation (the brown square represents the fourth generation); (d) summary of results after testing the fifth catalyst generation (the brown square represents the fifth generation).

this iteration procedure are as follows: (i) selection of the best experimental point (hit), (ii) variable position change, (iii) formation of a new experimental region, and (iv) testing. Accordingly, several further iterations is shown in Fig. 5. Fig. 5a shows the results of testing of the second generation after variable position change. Please note that the hit (see the small red square) has a completely new neighbourhood. In

this new neighbourhood a new experimental region is created (see the large brown square in Fig. 5a) and the third generation is tested resulting in a new hologram shown in Fig. 5b.

The test results of the fourth and fifth catalyst generation are shown in Fig. 5c and d. As emerges from these figures after each iteration the ratio of darker points increases significantly. It means that the process of optimisation is moving towards the direction to the optimum.

It can be added that in Figs. 4 and 5 an arbitrary set of variable position changes has been applied. In the given arrangement of variables after every four iterations the original position is generated again, i.e., the initial order of the variables is restored after the fourth step. Upon comparing Figs. 3b and 5d the clusters of the initial catalyst library, highlighted with black frames, can be recognised.

Summing up the main steps in HRS the importance of variable position changes has to be emphasised. The new catalyst generation has to be created in the new neighbourhood of the hit, consequently, variable position changes is the main driving force in the route to find the optimum.

3.2. Virtual catalytic experiments with eight variables

Let us demonstrate the performance of the HRS in an eight-dimensional experimental space with about 60 000 potential experimental points. In the hypothetical parameter space upon using the objective function (1) catalysts were prepared from eight possible metallic components. In the hologram the content of Pt, Pb, Sn, and In were placed along the *X*, while that of, Ga, Ge, Ru, Pd along the *Y*-axis, respectively. Our objective function (1) describes the relationship between the composition of catalysts and the conversion in CO oxidation.

The initial library was created along the symmetry elements resulting in 48 experimental points in the first catalyst generation. Upon using HRS each new generation of catalysts was "prepared" using an experimental region of size 4×4 around the local optimum. Every experimental point has been tested resulting in maximum 16 catalyst in each iteration step. The results of these iteration steps are given in Table 3. The best catalyst (the lead) obtained after 153 virtual tests consists of three components: platinum, palladium and tin. The complete analysis of the experimental space described by Eq. (1) showed that in the 9th iteration step the global optimum has been found.

In this optimisation procedure each 8th consecutive variable position change resulted in the same order of variables along axes. Accordingly, if after the 17th $(9 + 8)$ iteration the value of the objective function remains unchanged it can be concluded that the global maximum has been found. The results of these additional iterations are also shown in Table 3 demonstrating that in the present optimisation the global optimum has been found after 153 hypothetical experiments.

Table 3
Summary of the holographic optimisation with an experimental region of size 4×4 using the objective function (1)

Steps	Number of experiment	Composition of the best catalysts (wt.%)								Conversion (%)
		Pt	Pb	Sn	In	Ga	Ge	Ru	Pd	
1	48	2.1	0.8	0.0.	0.0	0.3	0.0	0.0	0.5	10.67
2	62	2.1	0.8	1.1	0.0	0.3	0.0	0.2	0.5	22.83
3	76	2.1	0.8	1.5	0.0	0.3	0.0	0.2	0.5	25.62
4	88	2.1	0.8	1.5	0.0	0.0	0.0	0.2	0.5	29.28
5	100	2.1	0.8	1.5	0.0	0.0	0.0	0.0	0.5	30.33
6	114	2.1	0.8	1.5	0.0	0.0	0.0	0.0	1.4	44.15
7	128	2.1	0.6	1.5	0.0	0.0	0.0	0.0	1.4	49.39
8	139	2.1	0.3	1.5	0.0	0.0	0.0	0.0	1.4	57.19
9	153	2.1	0.0	1.5	0.0	0.0	0.0	0.0	1.4	64.99
10	167	2.1	0.0	1.5	0.0	0.0	0.0	0.0	1.4	64.99
⋮										
17	209	2.1	0.0	1.5	0.0	0.0	0.0	0.0	1.4	64.99

It has to be mentioned that the optimum found above belongs to the given resolution of the experimental variables. Further improvement in the "catalytic activity" can only be attained by establishing new intervals for the variables, most practically around the present optimum. It allows refining the resolution as well, i.e., reducing the distance between the discrete values of a variable. Similar approach is also accepted in the classical factorial DOE method [4].

In HRS the size of the experimental region has a great importance, too. Additional experimental regions can also be selected around the second and the third best experimental points. Upon using this approach more and more experimental points can be measured resulting in more information about the experimental space as it is shown in Fig. 6a–d. Fig. 6a–d shows the holograms after "measuring" 209, 389, 911, and 2898 experimental points. These holograms were obtained upon using experimental regions in size 4×4 around

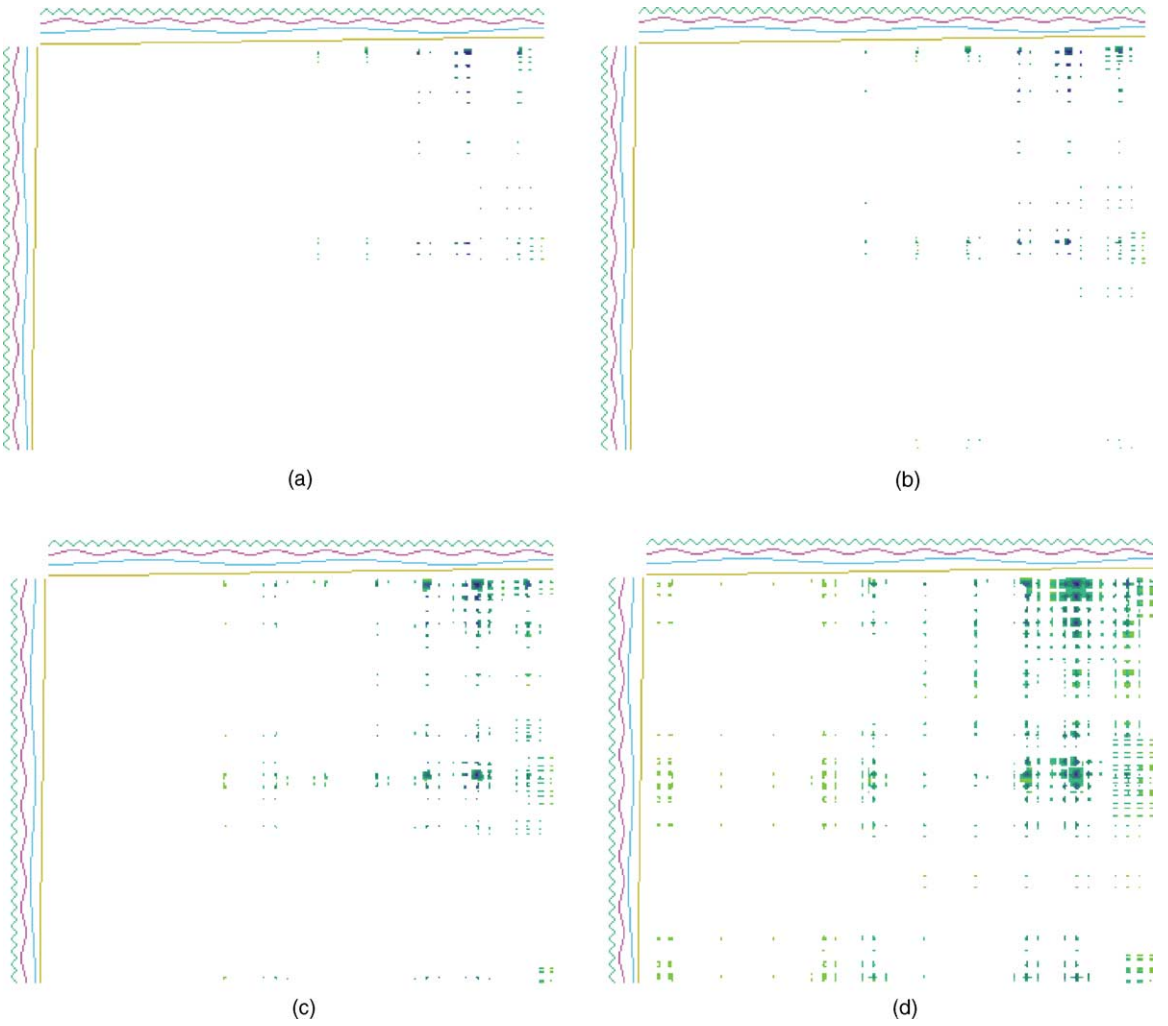

Fig. 6. The experimental space described by the objective function (1) after testing different number of "virtual catalysts"; a, b, c, and d—results after 209, 389, 911 and 2898 "virtual" catalytic runs, respectively. Variable are designated as follows: along the *X*-axis ▬ Pt, ▬ Pb, ▬ Sn, ▬ In; along the *Y*-axis ▬ Ga, ▬ Ge, ▬ Ru, ▬ Pd. Colour code of the activity data ranges are as follows: ▫ 0–13%, ▪ 13–26%, ■ 26–39%, ■ 39–52%, ■ 52–65%.

the best experimental point; 5×5 and 4×4 around the best two experimental points; 7×7, 6×6, 5×5 and 4×4 around the best four points; 13×13, 11×11, 9×9, 8×8, 7×7, 6×6, 5×5 and 4×4 around the best eight points, respectively. Having measured about 3000 experimental points it can be seen that the density of the experimental points in the vicinity of the global optimum increases.

The holograms shown in Fig. 6a–d clearly show the importance of platinum. With increasing Pt content the conversion increases. The hologram shows also different periodical changes, which can be related to the frequency of different components. The broad bands along the *X*-axis follow the periodicity of tin. It indicates a synergism between tin and platinum. Similar synergism between Pt and Pd can also be seen. The three bands along the *Y*-axis belongs to the minimum of Ge. Consequently, germanium has a negative effect on the conversion. As a conclusion, Fig. 6a–d clearly demonstrates that the geometric arrangement in the hologram partially reveals the composition–activity relationship.

Fig. 7 represents the whole experimental space. The total number of catalysts shown is 81 920 but catalysts with more than 6 wt.% metal content have not been involved in the optimisation procedure used. Comparing Figs. 6a-d and 7 it can be concluded that in the region far away from the optimum only sporadic measurements were done. This observation indicates that the algorithm used avoids experimental points that are far away from the optimum.

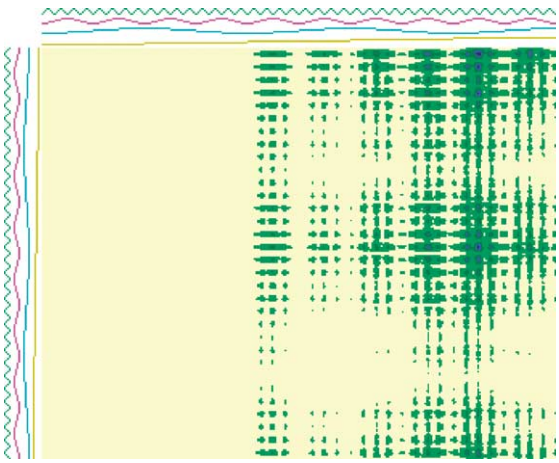

Fig. 7. The whole experimental space described by the objective function (1).

The presentation of the whole experimental space shows more defined periodicity in the catalytic activity. Within this periodicity different local maxima can also be seen. It has to be emphasised again that without variable position changes the algorithm would stop after few iterations finding only one of the local maxima.

4. Conclusions

Results obtained in this study clearly indicated that

(i) the continuous multidimensional experimental space can be transformed into a two-dimensional hologram;
(ii) in the hologram in the neighbourhood of any experimental point there are points which differ from each other only slightly in properties;
(iii) the holographic arrangement of experimental points provides clear visualisation of the whole experimental space;
(iv) the geometry of the experimental points reveals qualitatively the composition–activity relationships.

Results obtained so far show that the HRS is a powerful optimisation method. It is a very effective tool in catalyst library design. In an eight-dimensional space less than 200 measurements are sufficient to find the optimum.

Before to start the HRS optimisation the following parameters have to be fixed:

(i) the number of components of the initial catalyst library;
(ii) the parameter levels of each components;
(iii) the number of best experimental points (centres) used in the optimisation procedure;
(iv) the size of the experimental regions around the best data points;
(v) the way of variable transformations.

These sets determine unequivocally the route of optimisation, i.e., the position of measured experimental points in the given experimental space. In this way the investigated parameter, obtained either from an arbitrary objective function or from a real measurement,

reaches its optimum passing always through the same data points. Therefore, HRS is considered as a deterministic and not a statistical, multivariate optimisation method. This is in contrast to the GA, where using the same settings (e.g. size of the population, number of generations, the rate of qualitative and or quantitative mutation is fixed) different catalysts can be tested in each simulation [6].

References

[1] P.P. Pescarmona, J.C. Waal, I.E. Maxwell, T. Maschmeyer, Catal. Lett. 63 (1999) 1.
[2] B. Jandeleit, D.J. Schaefer, T.S. Powers, H.W. Turner, W.H. Weinberg, Angew. Chem. Int. Ed. 38 (1999) 2494.
[3] S. Senkan, Angew. Chem. Int. Ed. 40 (2001) 312.
[4] N. Rueda, R. Bacaud, P. Lanteri, M. Vrinat, Appl. Catal. A 215 (2001) 81.
[5] A.A.G. Lima, M. Nele, E.L. Moreno, H.M.C. Andrade, Appl. Catal. A 171 (1998) 31.
[6] D. Wolf, O.V. Buyevskaya, M. Baerns, Appl. Catal. A 200 (2000) 63.
[7] A.S. McLeod, L.F. Gladden, J. Chem. Inf. Comput. Sci. 40 (2000) 981.
[8] A. Tejfalussy, HU Patent 194 997 (1983).