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Discovery of new paraffin isomerization catalysts based on SO_4^{2-}/ZrO_2 and WO_x/ZrO_2 applying combinatorial techniques

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Abstract

Applying accelerated techniques for catalyst synthesis and testing and a stochastic experimental design, two catalytic systems based on SO_4^{2-}/ZrO_2 and WO_x/ZrO_2 were seen as active and selective for *n*-paraffin isomerization. After three optimization cycles, a new catalyst formulation based on promoted SO_4^{2-}/ZrO_2 with improved activity and selectivity has been found. Characterization of the best catalysts generated in each cycle has been done. Activity and selectivity of the best catalyst found has been tested in the isomerization of a simulated industrial feed composed by *n*-pentane, *n*-hexane and *n*-heptane. For the second best catalytic system, i.e. WO_x/ZrO_2, the influence of tungsten content, promotor (Ce), nature of the starting precursor salt (sulfate, nitrate or chloride), and catalyst calcination temperature was studied using a factorial design. The relevance of the interaction between salt precursor and calcination temperature is discussed.

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1. Introduction

The optimization of heterogeneous catalysts for a specific process is mostly achieved by the systematic variation of the catalyst formulation (active metals, nature of the support) and preparation conditions. In traditional research processes, the catalysts are frequently tested one-at-a-time by using laborious and time-consuming catalytic methods.

Combinatorial methods [1–4] are applying accelerated (high-throughput) techniques, which allow the preparation and characterization/catalytic testing of a large number of new materials in a parallel way at lower scale than traditional. Hence, combinatorial methods enable to increase the number of catalytic parameters to be screened minimizing the research time and costs.

The combinatorial approach combines the use of high-throughput experimentation (HTE) techniques with the application of new optimization strategies, allowing a more efficient experiment design [5–9]. This strategy directs the search process and decides which materials have to be prepared considering the testing results of the already tested materials. In this sense, a generalized approach employs a genetic algorithm (GA) [9–12] as a search strategy in order to optimize the catalyst composition. This optimizing strategy (GA) is quite appropriate for heterogeneous catalysis since: (i) GA tolerates noisy data (experimental data) with considerable error; (ii) GA uses a

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population of points to conduct the search, what fits quite well with the application of HTE techniques; and (iii) the goal is to find an approximate maximum in a high-dimensional space minimizing the number of trials.

This GA approach looks for combinations of elements and concentrations, which would deal better experimental results. Through the search process, the combinatorial procedure focuses on specific regions (exploitation) of the whole combinatorial space in which catalyst results are supposed to be more promising. On the other hand, the combinatorial procedure tries to preserve the diversity up to a point, exploring different regions (exploration). All this is carried out by applying conveniently the GA operators: *crossover* for exploitation and *mutation* for exploration.

Combinatorial methods are generally applying [5,6,13] the catalytic reaction assay as the unique experimental *output* of the catalysts and, in many cases, that assay only allows the catalyst optimization without extracting much more information about the principles of catalysis itself, in other words, about the science behind the optimization process, structure–activity relationship for instance. With this aim, catalyst characterization was introduced as experimental part within a combinatorial search.

In the present work, we have applied the GA methodology to the discovery of new active catalytic formulations for hydroisomerization of *n*-alkanes. The hydroisomerization of light paraffins (C_5, C_6, C_7) to produce its branched isomers is an important industrial process that it is used to produce gasoline of high octane number. Legislation pressures for the lead additive, olefins and aromatics phase-out from gasoline [14,15] have made of isomerization an interesting alternative process for this purpose.

The isomerization of light paraffins is an acid-catalyzed process, in which the equilibrium shifts to low octane *n*-paraffins when reaction temperature increases (Fig. 1). Thus, isomerization temperature has to be reduced as much as possible in order to maximize the yield of dimethyl-alkanes. At present, the isomerization is industrially carried out on catalysts such as halogen-treated alumina or mordenite zeolite. The former catalyst works at lower reaction temperature but it is highly corrosive, difficult to handle and very sensitive to sulfur and water poisoning. Mordenite-based catalysts are more resistant to water and sulfur but require higher

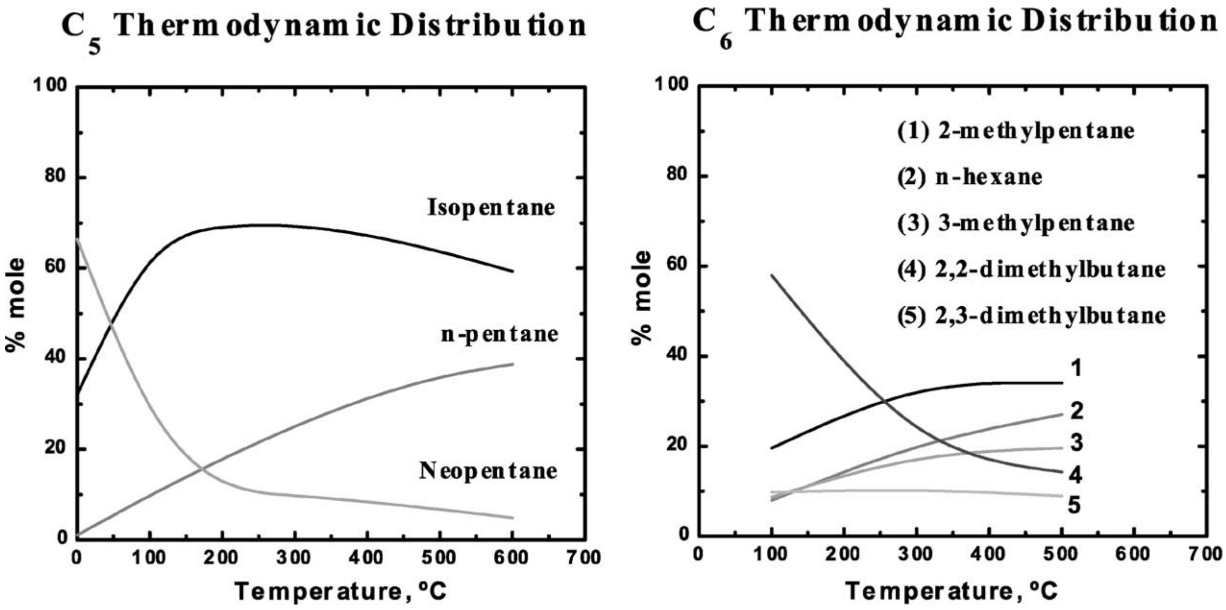

Fig. 1. Influence of temperature on the thermodynamic distribution of pentane and hexane isomers.

reaction temperature with the corresponding penalty in octane.

Considering this scenario, it would be interesting to develop a new generation of environmentally friendly catalysts with high activity and selectivity to branched isomers and low working temperature.

About 25 years ago, it was shown that by a sulfate treatment of oxides such as ZrO_2, TiO_2, SnO_2, Fe_2O_3 and HfO_2, a remarkable increase in the surface acidity and in the catalytic activity for carbenium ion reactions was achieved [15–22].

In the first part of this work, a screening of different basic oxide formulations has been made employing a GA, a multiple reactor system and characterization equipment. Two final catalytic systems have been optimized, i.e. SO_4^{2-}/ZrO_2 and WO_x/ZrO_2. Finally, the best formulations have been tested using a simulated industrial feed for comparison with traditional isomerization catalysts.

2. Experimental

2.1. Methodology

2.1.1. Catalyst formulation

In the present study case, we have classified the pool of possible catalyst components in three groups: metal oxide support, acidity enhancers and promotors: (a) metal oxide supports—γ-Al_2O_3, ZrO_2 and TiO_2; (b) acidity enhancers—SO_4^{2-}, BO_3^{3-}, PO_4^{3-} and WO_x, the content of SO_4^{2-}, BO_3^{3-}, PO_4^{3} is ranging from 0.5 to 6 wt.%, and from 0.5 to 36% for WO_x; (c) promotors—Pt, Ce, Pd, Sn, Ni, Mn and Nb, the content of each metal is ranging from 0.5 to 6 wt.%. Each material contains one support, one acidity promotor and at least two metallic promotors, from which one is Pt (0.5 wt.%).

2.1.2. Structure of the search algorithm

The genetic algorithm is initialized by generating 24 catalyst compositions, random combinations of the established catalytic parameters following the patterns explained above. Succeeding generations were set up by the genetic algorithm taking into account the catalytic performances of the previous generation, applying crossover and mutation operators. The objective function is derived from experimental values of selectivity (S) to *iso*-pentane and *n*-pentane conversion (X). The population size is 24 catalysts, that is, the 0.167% of the ab initio solution space. An elitism approach is also used, so that the new generation includes the offspring of the selected and the very best compositions of the last generation.

2.2. Catalyst preparation

A crucial factor in the optimization of catalysts is the preparation procedure, since little variations in those conditions would change severely the final phase of the solid and consequently its catalytic characteristics. Many parameters could be set as variables for the genetic algorithm but this would require again an intensive experimental work. Typical preparation variables are promotor precursors, type of impregnation, calcination atmosphere, time, temperature, reduction time and temperature and so forth. The preparation method used in the present study is explained below.

2.2.1. Metal oxide supports synthesis

Zirconium hydroxide was prepared by precipitating from a 0.4 M aqueous solution prepared by zirconium(IV) oxide chloride $ZrOCl_8{\cdot}H_2O$ (Riedel-de Haën) with an excess of NH_4OH to a final pH of 8.3. After, the precipitate is washed with distillate water to complete Cl^- elimination and dried at 160 °C for 16 h.

Titanium hydroxide was prepared by precipitating from a solution of titanium isopropoxide in nitric acid (molar ratio 1:1) with an excess of NH_4OH to final pH of 7. After the precipitate is filtered, washed with distillate water and dried at 160 °C for 16 h.

γ-Aluminia was a commercial product from Merck.

2.2.2. Acidity enhancers precursors

Four acid enhancers were used to generate acidity over the metal oxide supports. The precursor used were: $(NH_4)_2SO_4$, H_3BO_4, H_3PO_4 and $(NH_4)_6H_2W_{12}O_{40}{\cdot}nH_2O$.

2.2.3. Promotor precursors

Promotors precursor used for the impregnation were: $Ni(NO_3)_2{\cdot}6H_2O$, $MnCl_4{\cdot}4H_2O$, $SnCl_4{\cdot}5H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$, $PdCl_2$, $C_{10}H_5O_{20}Nb{\cdot}H_2C_2O_4$ and H_2PtCl_6.

The precursors used for the study of cerium were: $Ce(NO_3)_3$, $Ce(SO_4)_2$ and $CeCl_3$.

2.3. Parallel impregnation procedure

The different promotors were incorporated to the corresponding supports by incipient wetness impregnation following an automated impregnation procedure. A robotic system was employed, which enables to dose and weight different solids and liquids, handle different types of vials and vortex stir. The preparation was carried out in parallel for each generation applying a sequential impregnation procedure. The followed steps carried out by the automated system included: (i) impregnation of the different supports with the acidity enhancer precursor solutions and subsequently drying at 160 °C for 16 h; (ii) impregnation with the promotor precursor (except Pt) solutions and drying at 160 °C for 16 h; and (iii) final impregnation with H_2PtCl_6 (Pt 0.5 wt.%) and drying at 160 °C for 16 h. The final materials are then composed of one oxide support impregnated with one acidity enhancer, one promotor and platinum.

2.4. Catalytic testing

High-throughput testing was accomplished using a system of 16 continuous fixed-bed parallel microreactors, able to work up to 80 MPa. Feeding of gases and liquids in each reactor was carried out and measured independently. Temperature and pressure is measured in each catalyst bed. Catalysts calcination and reduction was performed in the same testing system prior to reaction test.

Calcination is performed at 600 °C under airflow for 8 h and reduction at 250 °C for 2 h under hydrogen flow. The catalytic tests were carried out at 3 MPa total pressure, temperature range 200–240 °C and 2.26 h^{-1} WHSV, H_2/hydrocarbons molar ratio of 2.93. The amount of catalyst in each fixed-bed microreactor is 500 mg and particle size 0.4–0.6 mm, for which there are not internal diffusion limitations. Reaction products distribution was analyzed on-line by using a gas chromatograph (Varian 3380GC) equipped with a Plot Alumina capillary column.

2.5. Catalyst characterization

The structure and the crystallinity of solids were determined by X-ray diffraction on a Phillips PW diffractometer using Cu Kα radiation. Surface measurements were obtained on a ASAP-2000 apparatus following the BET procedure.

The acidity of these materials was measured by temperature-programmed desorption (TPD) of NH_3 on a TPD/TPR 2900 equipment (Micromeritics). For these experiments 200 mg of catalysts were pre-treated in oxygen flow at 550 °C for 3 h followed by nitrogen for 30 min. Then, ammonia was adsorbed at 100 °C until saturation and afterwards desorbed from 100 up to 600 °C in a helium flow at a heating rate of 10 °C min^{-1}. The amount of ammonia desorbed was monitored by means of a thermal conductivity detector (TCD). Blank runs under the same experimental conditions were also performed and subtracted from the corresponding TPD diagrams.

Sulfur analysis was done employing a Perkin-Elmer 2400 CHNS analyzer.

3. Results and discussion

3.1. Genetic algorithm search process

The compositions of the different generations were designed applying a stochastic algorithm. Each catalytic material consisted of three components (one support + one acidity enhancer + promotors) having each catalyst set of 24 new materials, see, for instance, the compositions shown in Table 1 for the most active catalyst of each generation. Each catalyst set was synthesized and tested for the *n*-pentane isomerization according to the methods described above. After each reactivity evaluation, the optimization algorithm designed the next set of catalyst taking into account the compositions and catalytic performances of the prior generation of catalysts. For *n*-pentane isomerization, the objective functions were conversion and branching selectivity. However, owing to the absence of cracking, selectivity to methylbutane is practically 100% and consequently conversion becomes the only objective function.

In the present study, three evolving cycles have been run, that means that three catalysts generations (72 samples) have been prepared and tested. Fig. 2 shows the catalytic performances of the 10 most active catalysts for the three succeeded generations at three different reaction temperatures. An important improvement in the activity can be observed during

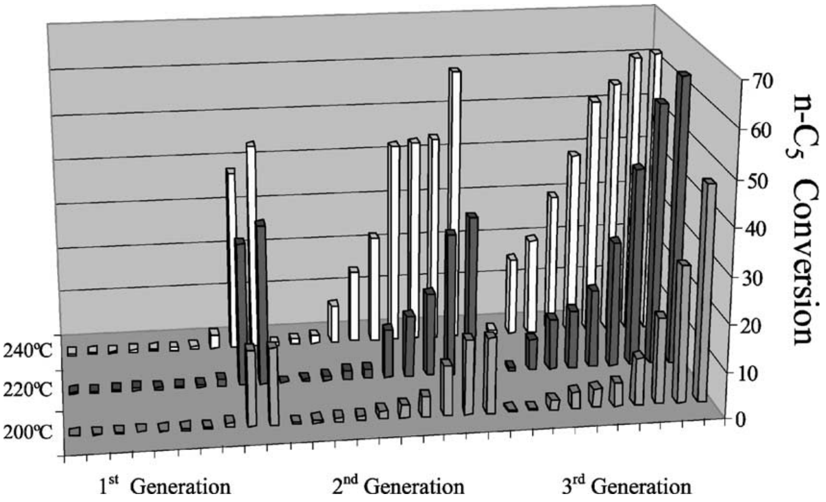

Fig. 2. Isomerization catalytic performance (n-pentane conversion) of the 10 best-ranked materials of three generations at three temperatures (500 mg catalyst, 2.26 h^{-1} WHSV, 200–240 °C, $H_2/n\text{-}C_5 = 2.93$ and 3 MPa).

the *evolution*. After three runs, the search process has been focused on the ZrO_2-S area where the catalyst based on ZrO_2-S-Nb-Pt exhibits the highest activity, although it cannot be asserted that this maximum is the absolute maximum of the solution space. By means of this optimization process, a substantial improvement in the catalytic materials has been achieved. However, it was of particular interest to characterize systematically the most active catalysts of each generation in order to determine the changes in the physico-chemical properties, responsible for the increase in activity and, therefore, for driving the search algorithm to the observed optimum. Characterization was carried out using conventional apparatus.

The crystallization and stabilization of the oxides ZrO_2, TiO_2 and Al_2O_3 in the crystalline phases tetragonal, anastasa and gamma, respectively, allow to obtain oxides with good catalytic properties in light paraffin isomerization [23,24]. XRD results for the 10 best-ranked catalysts of each generation show that these active phases are the majority in all materials and do not exist important differences from the first to the last generation. Acidity enhancers (BO_4^{3-}, WO_x, SO_4^{2-} or PO_4^{3-}) have been introduced in the general catalyst formulation to promote the stabilization [25] of these phases in the support. From the XRD results, it can be said that the amount of enhancers used are enough to achieve the desired phase stabilization. However, the improvement in catalytic activity, observed during the evolution process, cannot be explained considering uniquely the stabilization of these phases observed by XRD analysis.

Catalyst surface area was determined by the BET method. For a comparative study of these results we have considered three different groups: (a) catalysts based on zirconia (Z); (b) catalysts based on alumina (A); and (c) catalysts based on titania (T). Fig. 3 shows

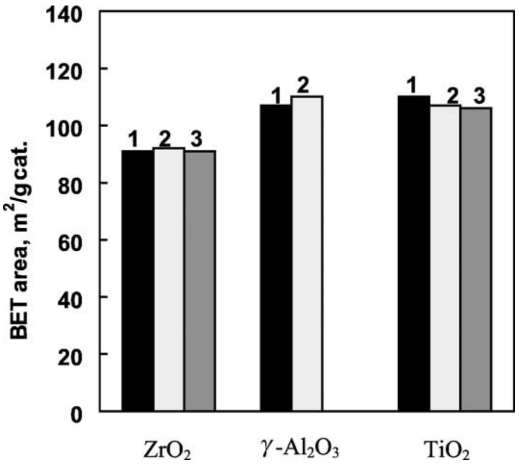

Fig. 3. BET area results for the 10 most active materials of each generation: (1) first, (2) second, and (3) third generation for the three groups of supports.

Table 1
Composition of the 10 best catalytic materials of the three successive generations

	Support	Acidity enhancer (wt.%)	Promotor (wt.%)
First generation			
1	ZrO_2	S (1.75)	Ce (0.97), Pt (0.51)
2	ZrO_2	S (2.18)	Pd (1.00), Pt (0.46)
3	TiO_2	W (17.38)	Mn (0.87), Pt (0.48)
4	ZrO_2	W (5.58)	Ni (0.55), Pt (0.51)
5	Al_2O_3	W (45.57)	Nb (4.60), Pt (0.52)
6	Al_2O_3	W (11.27)	Sn (5.52), Pt (0.47)
7	ZrO_2	B (0.54)	Ni (1.06), Pt (0.50)
8	ZrO_2	P (4.34)	Mn (3.90), Pt (0.48)
9	TiO_2	B (0.55)	Mn (0.97), Pt (0.55)
10	Al_2O_3	S (2.5)	Mn (1.09), Pt (0.51)
Second generation			
1	ZrO_2	S (2.22)	Pd (0.49), Pt (0.47)
2	ZrO_2	S (1.76)	Ce (0.97), Pt (0.51)
3	ZrO_2	S (2.57)	Nb (4.05), Pt (0.47)
4	ZrO_2	S (2.05)	Mn (1.74), Pt (0.48)
5	ZrO_2	B (2.33)	Mn (1.86), Pt (0.51)
6	Al_2O_3	P (1.42)	Mn (7.87), Pt (0.52)
7	TiO_2	P (3.72)	Ce (0.94), Pt (0.49)
8	TiO_2	S (2.55)	Ni (2.05), Pt (0.49)
9	TiO_2	S (1.98)	Ce (0.86), Pt (0.51)
10	Al_2O_3	W (39.18)	Ce (0.68), Pt (0.49)
Third generation			
1	ZrO_2	S (2.21)	Nb (0.48), Pt (0.56)
2	ZrO_2	S (2.15)	Ce (1.18), Pt (0.48)
3	ZrO_2	S (0.59)	Pd (0.52), Pt (0.56)
4	ZrO_2	S (1.81)	Nb (5.11), Pt (0.42)
5	ZrO_2	S (2.44)	Nb (3.96), Pt (0.52)
6	ZrO_2	S (2.63)	Ce (1.10), Pt (0.47)
7	ZrO_2	S (2.55)	Nb (0.88), Pt (0.48)
8	ZrO_2	S (2.09)	Mn (1.13), Pt (0.48)
9	ZrO_2	P (3.32)	Nb (1.01), Pt (0.44)
10	TiO_2	S (2.62)	Ce (0.52), Pt (0.48)

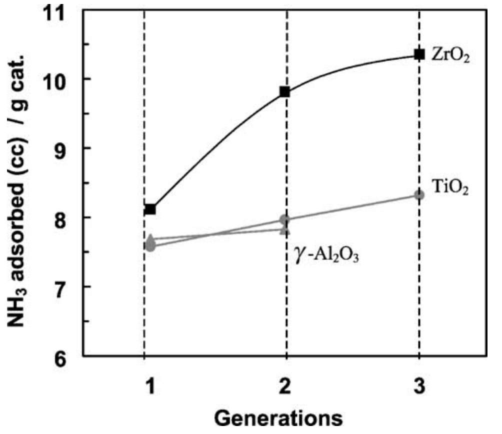

Fig. 4. TPD-NH_3 results for the 10 most active materials of each generation: (1) first, (2) second, and (3) third generation for the three groups of supports.

the evolution of the average area for each group, being clear that the observed improvement in activity within the different catalyst generations does not correlate either.

Acidity measurements were carried out by TPD-NH_3. Fig. 4 represents the average acidity for each of the above group, expressed in adsorbed NH_3 volume (cm^3) per catalyst gram. A gradual increase in the NH_3 absorption can be observed through the evolution process. The catalyst acidity is related directly with the catalytic activity in isomerization reaction and the higher activity found can, therefore, be attributed to the increase of acidity achieved by the new combination of promotors over the supports (zirconia).

3.2. *Validation of the best catalytic system*

The most active formulation (Z-S-Nb-Pt) was tested in a conventional reactor using as a feedstream a mixture of light *n*-alkanes (*n*-pentane 20 wt.%, *n*-hexane 60 wt.% and *n*-heptane 20 wt.%) simulating an industrial LSR stream. The experiments were carried out in a conventional reaction system using a fixed-bed continuous-flow reactor. Reaction was carried out at 3 MPa of total pressure, 2.26 h^{-1} WHSV, H_2/hydrocarbons molar ratio of 2.93, and 160 °C of reaction temperature. The activity and selectivity of this catalyst (Fig. 5) are compared with those obtained with sulfated zirconia impregnated with platinum (S-Z-Pt). Fig. 5 represents the evolution of the conversion with reaction temperature. There can be observed that the reactivity of the *n*-paraffin follows the order *n*-heptane > *n*-hexane > *n*-pentane for both catalysts, as it was expected taking into account the adsorption heats of the different hydrocarbons [26].

S-Z-Nb-Pt catalyst shows a higher isomerization selectivity and activity for all hydrocarbons. While *n*-pentane and *n*-hexane isomerization selectivity is very similar with both catalysts, important differences can be observed in the case of *n*-heptane. Indeed, S-Z-Nb-Pt exhibits a *n*-heptane isomerization selectivity of ∼50% at ∼60% of conversion, while the

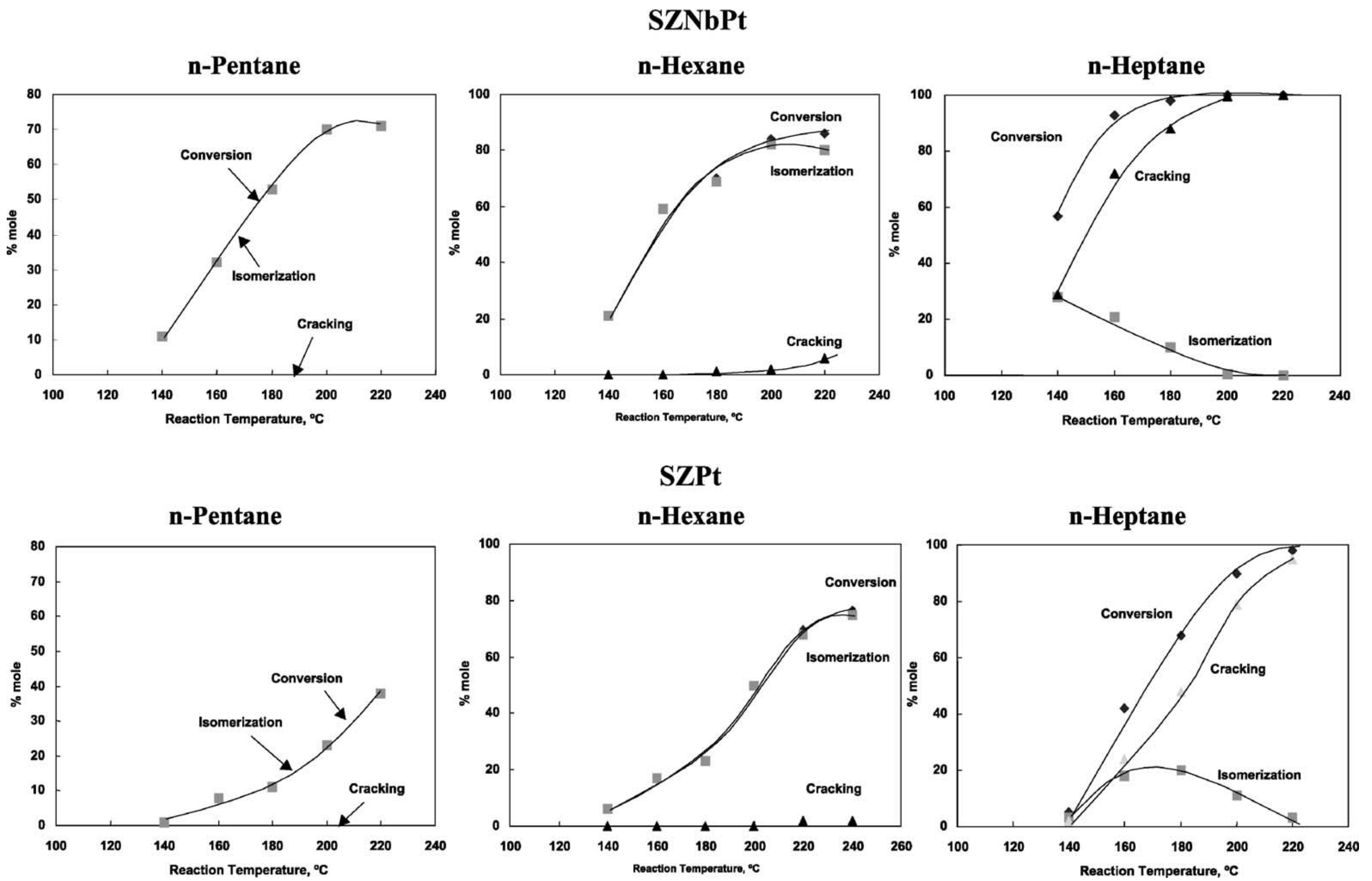

Fig. 5. Isomerization performance (conversion, and yield to isomerization and cracking) of n-C_5, n-C_6 and n-C_7 over conventional sulfated zirconia (S-Z-Pt), the new sulfated zirconia formulation (S-Z-Nb-Pt) and Pt-mordenite catalyst. Reaction conditions: 2.26 h^{-1} WHSV, H_2/hydrocarbons molar ratio of 2.93, 3 MPa total pressure and feed composition n-C_5/n-C_6/n-C_7 = 2/6/2 wt.

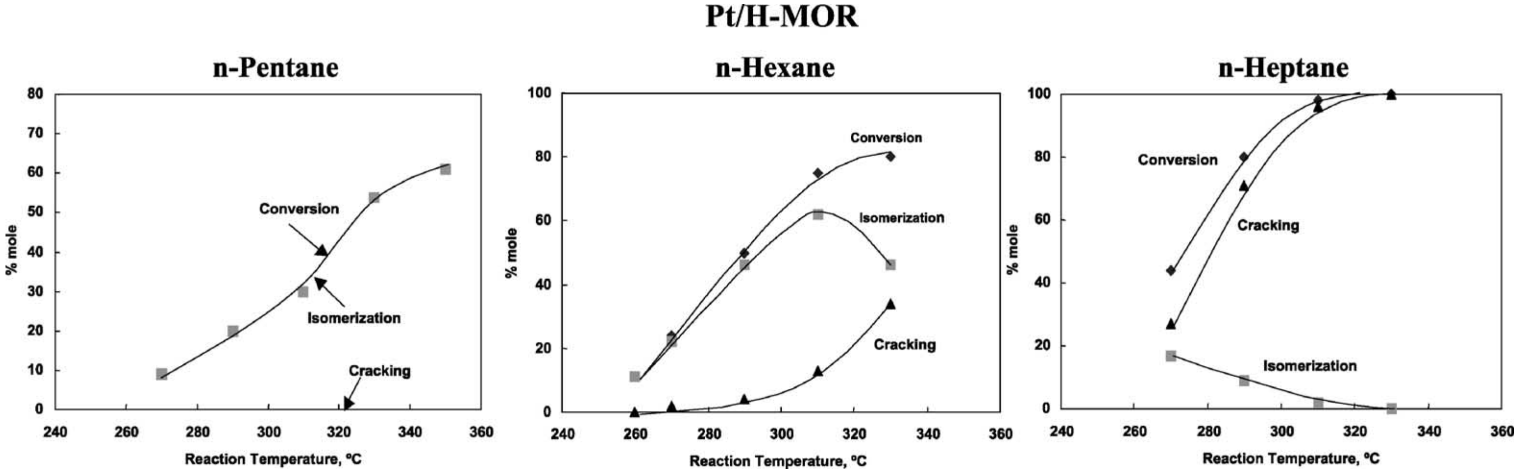

Fig. 5. (*Continued*).

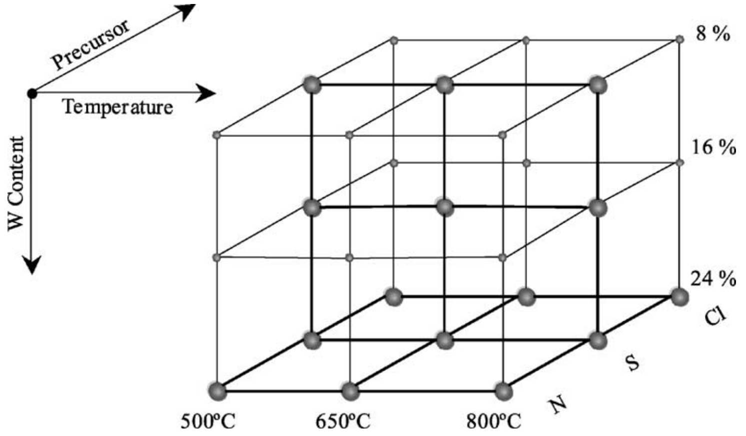

Fig. 6. Experimental design for three-level study of three variables: content of tungsten (wt.% W), calcination temperature and precursor salt (nitrate, sulfate and chloride).

selectivity obtained with S-Z-Pt at the same conversion level is only ∼30%. However, when high conversions of *n*-pentane and *n*-hexane are reached on S-Z-Nb-Pt, the *n*-heptane selectivity becomes very low.

In Fig. 5, it is also plotted the catalytic results obtained on an industrial practiced Pt-mordenite-based catalyst. In comparison with the new S-Z-Nb-Pt formulation, Pt-mordenite catalyst is much less active for light *n*-paraffin isomerization but also much less selective for *n*-heptane isomerization.

3.3. Study of the system Zr-W-Ce-Pt

A detailed study of the catalytic results achieved by the GA methodology shows that catalysts based on Zr-W-Pt exhibit a significant activity but still lower than those reported in previous works [27]. WO_x/ZrO_2 system is a well-known high activity material able to isomerize light alkanes at low temperatures [28]. For this reasons, a systematic study of this system (Zr-W-Ce-Pt) was performed to achieve a better understanding of the variables which are determining the final isomerization activity. The variables studied were: calcination temperature, tungsten content and nature of the promotor precursor salt, i.e. sulfate, nitrate and chloride. Cerium promotor has been selected since a Z-S-Ce-Pt formulation shows a very high activity (second ranked lead) and different Ce precursors salts are available compared with Nb precursors.

If a three-level factorial design [29] is considered for the study of the influence of these three variables, the test of 3^3 samples would be required (see Fig. 6). For practical reasons, we have selected for this study two building blocks of the whole 3^3 design, corresponding with two 3^2 factorial designs, reducing the total number of samples to 15. These materials were tested for isomerization activity in the multiple reactor (calcinations ex situ) using as feedstream a mixture of *n*-pentane and *n*-hexane (60–40 wt.%), 240 °C, 3 MPa, 2.26 h^{-1} WHSV, H_2/hydrocarbons molar ratio of 2.93.

The levels for each variable were selected taking into account previous works: (i) calcination temperatures [30–34]—500, 650 and 800 °C; (ii) tungsten content [30–34]—8, 16 and 24 wt.%; and (iii) Ce precursor nature [35–37]: sulfate, nitrate and chloride.

3.3.1. Influence of precursor salt and calcination temperature

The catalytic performance (*n*-alkane conversions (%)) of these first 3^2 materials is displayed in Fig. 7. The most active materials are those calcined at 800 °C, being, in this case, the Ce precursor salt of minor relevance for the isomerization activity. However, when comparing the samples calcined at 650 °C, the sample prepared with Ce sulfate as precursor presents a much higher activity than the other two. A reason for that, is that part of the sulfate interacts with the zirconia, remains in the catalysts and improves its acidity.

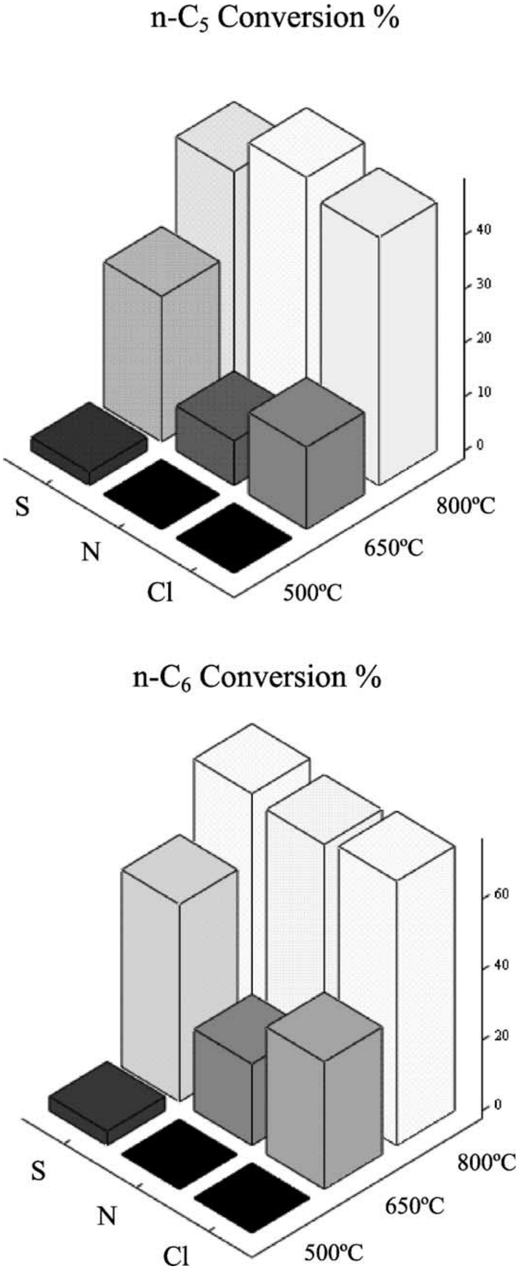

Fig. 7. Catalytic results for study of calcination temperature and promotor precursor in the Zr-W-Ce-Pt system. Reaction conditions: 2.26 h^{-1} WHSV, H_2/hydrocarbon molar ratio of 2.93, 3 MPa, 240 °C and feed composition n-C_5/n-C_6 = 6/4 wt.

Table 2
Sulfur analysis of the different WO_x/ZrO_2 materials

W (wt.%)	Ce precursor	S (wt.%)		
		Before calcination	After calcination	
			650 °C	800 °C
24	Sulfate	0.46	0.28	0
16	Sulfate	0.46	0.39	0
8	Sulfate	0.46	0.36	0

However, when this material is calcined at 800 °C, all the sulfate is lost (see sulfur content in Table 2) and the acidity is only due to the tungsten effect. For low calcination temperatures (500 °C), the samples obtained are inactive indicating that these temperatures are too low to produce active sites to isomerize light alkanes.

3.3.2. *Influence of tungsten content and calcination temperature*

This 3^2 subset implies the variation of the tungsten content and calcination temperature maintaining fixed cerium sulfate as precursor. Catalytic results are represented in Fig. 8. The most active material is obtained for 16 wt.% W and 650 °C. However, the activity obtained for the same composition calcined at 800 °C exhibits also a high activity, being then a hypothetical maximum located in the area between both calcination temperatures (see white area of Fig. 8). The presence of a maximum can be explained considering that, when increasing the temperature the formation of W-based acid sites is promoted whereas the S-based acid sites disappear. In this sense, Table 2 shows that the samples calcined at 800 °C do not content S while those samples calcined at 650 °C content an amount of S close to the amount introduced during the impregnation.

3.3.3. *Promoting effect of cerium*

Fig. 9 compares the catalytic performance of one of the best Zr-W-Ce-Pt formulations (sulfate precursor, 16 wt.% W, 1 wt.% Ce, 0.6 wt.% Pt and 800 °C) and an optimized traditional tungsten zirconia formulation [37] (16 wt.% W, 0.6 wt.% Pt and 800 °C). The new Zr-W-Ce-Pt catalyst presents a higher isomerization activity, showing again a clear promoting effect of Ce, as was stated previously for Ce and Nb for the sulfated zirconia.

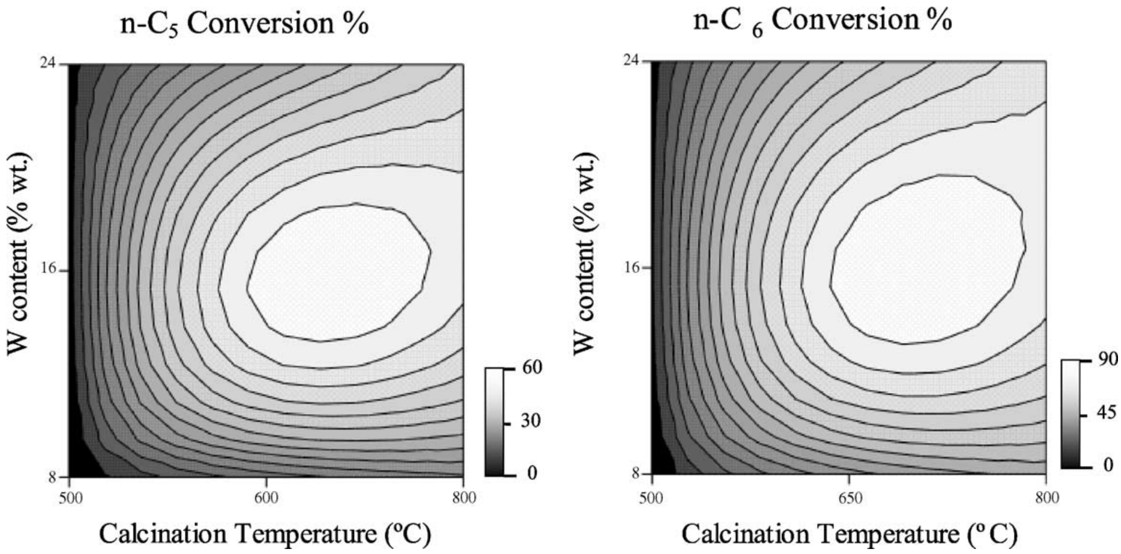

Fig. 8. Catalytic results for study of calcination temperature and W content in the Zr-W-Ce-Pt system. Reaction conditions: 2.26 h^{-1} WHSV, H_2/hydrocarbon molar ratio of 2.93, 3 MPa, 240 °C and feed composition n-C_5/n-C_6 = 6/4 wt.

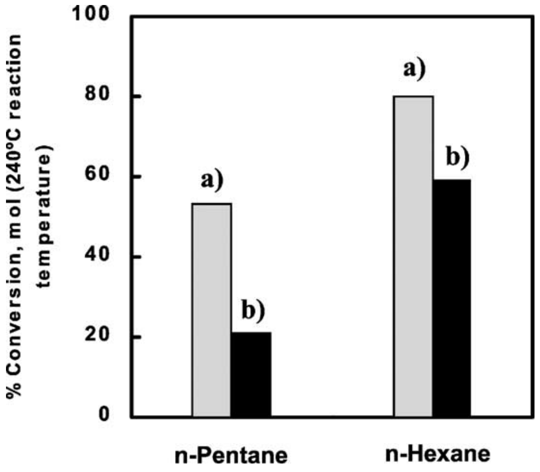

Fig. 9. Comparison of catalytic performances for two different tungsten zirconia formulations: (a) new formulation (sulfate precursor, 16 wt.% W, 1 wt.% Ce, 0.6 wt.% Pt and 800 °C); and (b) traditional formulation (16 wt.% W, 0.6 wt.% Pt and 800 °C). Reaction conditions: 2.26 h^{-1} WHSV, H_2/hydrocarbon molar ratio of 2.93, 3 MPa, 240 °C and feed composition n-C_5/n-C_6 = 6/4 wt.

4. Conclusions

A genetic algorithm and a factorial design have been applied to the search of new catalysts for the light paraffin hydroisomerization. The problem was initially focused by means of a knowledge-based catalyst formulation, in which each component (or series of components) was selected and incorporated to the catalyst formulation.

Though the number of evolving cycles is reduced, an important improvement in the catalyst activity has been found, being the catalytic performance even better than that exhibited by industrial practiced catalysts. Thus, a new catalyst formulation, based on sulfated zirconia, with higher activity and selectivity has been found. On the other hand, the parallel evaluation of their physico-chemical properties as crystal phases, surface area and acidity have helped to better understand the *catalytic evolution*.

The most active catalyst formulation (S-Z-Nb-Pt) has been tested using a mixture of *n*-paraffins as feed (*n*-pentane 20 wt.%, *n*-hexane 60 wt.% and *n*-heptane 20 wt.%) and the activity and selectivity of S-Z-Nb-Pt catalyst is higher than that of traditional S-Z-Pt and Pt-mordenite catalysts, particularly for *n*-heptane isomerization. The resultant catalyst is not able to isomerize *n*-heptane and high yields of cracking are found with this hydrocarbon.

A factorial design has been used to explore the second most active system found in the GA study, i.e.

Zr-W-Ce-Pt. In this case, it has been found that the nature of the salt for the promotor precursor plays an important role when calcination is done at 650 °C. Thus, sulfate is the preferred precursor and the sulfur remains at 650 °C. However, an absolute maximum in activity is found at 800 °C of calcination temperature regardless of the nature of the precursor salt. In any case, as predicted by the GA methodology, the SO_4^{2-}/ZrO_2-based system is more active than the optimum found for the WO_x/ZrO_2-based system.

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