Applying response surface design to the optimization of methane activation with ethane over Zn-H-ZSM-11 zeolite

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Abstract

Experiment design—response surface methodology (RSM) is used to model and to optimize the activation of methane (C1) using ethane (C2) as co-reactant into higher hydrocarbons, over Zn-containing zeolite catalyst. The application of this methodology allows a better understanding of the influence of the different factors: time on stream (TOS), space velocity of C2 (GHSV-C2), molar fraction of C1/(C1 + C2) (XC1) and reaction temperature, on the C1 conversion, reducing the operation costs, achieving efficiency and effectiveness of this process. Box–Behnken design was development with different levels of the factors, determining its influence on the C1 conversion in order to obtain responses surfaces. In this way, we found the best combination in the reaction parameters that allowed us to optimize the process. The results indicated that the reaction time, the XC1 and the interactions of the TOS–temperature factors, have the main influence on C1 conversion, in agreement with the experimental results reported previously.

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Keywords: Experiment design; Response surface; Optimization; Methane activation; Ethane co-reactant

1. Introduction

The natural gas (NG) constitutes a great energy source, economic and accessible, having an impact in the world energy balance, considered as an alternative source of fuel and other petrochemical products. Methane, the main component of the natural gas (up to 90% w/w depending on the source [1]), is the lowest paraffin and the hardest to activate in a chemical transformation because of its high stability and low reactivity. Methane is the most stable and symmetric organic molecule consisting of four C–H sp^3–s bonds with energy of 435 kJ/mol. The activation and the direct conversion of methane are a promising approach for the utilization of natural gas resource and also a great challenge in the science of catalysis. Methane direct transformation into aromatic hydrocarbons with participation of oxygen is thermodynamically favorable. However, the reaction of C1 with O_2 to form CO_2 and H_2O is thermodynamically much more favorable than the transformation of C1 into aromatics [2]. Han et al. [3] reported the direct partial oxidation of methane in the presence of propane to liquid hydrocarbons over HZSM-5 zeolite catalyst and at 960 psi. Methane conversion under non-oxidizing conditions is thermodynamically unfavorable although, high selectivity to non-oxygenated compounds can be obtained. Wang et al. [4] and Pierella et al. [5] reported C1 aromatization in the presence of small amounts of light hydrocarbons, under non-oxidizing conditions on transition metal ions supported on H-zeolites. ZSM-5 and ZSM-11 zeolites have been extensively studied as catalysts for aromatization of light paraffin [6–8]. Modified ZSM-zeolite material with Zn or Ga has successfully used for this purpose [9]. Inui [10] described the effect of these cations in the paraffin conversion. Anunziata et al. [11–13] have reported that Zn-ZSM11 shows an excellent aromatization behavior for ethane (C2), propane (C3), liquefied petroleum gas (LPG) and light gasoline (*n*-C5, *n*-C6 and *n*-C7). In previous works [5,14–16], the aromatization of C1 using various light paraffin as co-reactant was reported using Zn-ZSM11 catalyst. C1 would be activated under non-oxidizing condition by interaction with C2 and with LPG. Very high levels of C1 conversion to aromatic hydrocarbons were obtained by interaction with C2 (molar fraction in the feed: C1/(C1 + C2) = 0.4–0.8) over Zn-ZSM-11 (molar fraction $Zn^{2+}/(Zn^{2+} + H^+) = 0.86$) at 550 °C and total pressure of 1 atm, with the aromatic hydrocarbon yield

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between 10 and 40 mol% C1 [16]. Anunziata et al. [14] reported that, in the activation of C1 with LPG, aromatic hydrocarbons were the main products in the whole range of C1 molar fractions (0.4–0.85), reaching to higher levels of C1 conversion (10–45%).

The statistical experiments design is the process of planning an experiment to obtain appropriate data that can be analyzed by statistical methods, to produce concrete and valid conclusions. The objective of all experiment includes the descriptions of the responses to the treatment factors. The origin of the experiments design was in the twenties by the mathematician Fisher [17]; also Box [18–20], Cox [21], Kempthorne [22] and Cochran [23], have contributed on the design of experiments. Box and Wilson's work [18] and statistical methods, developed for modeling phenomena and to find combinations of a number of experimental factors led to most favorable response. One of the main advantages in the response curve is to visualize the response for all levels of the experimental factors [18]. Specifically, the response surface design is classified as a simultaneous method, being used in the stage of optimization [24]. Their application allows selecting the optimum combination of levels, to obtain the best response for a specific condition [25]. In the RSM, factorial designs are carried out and the results are adjusted using mathematical models. They are known as displacement and design stages, respectively; they are repeated several times, screening the response surface obtained in the direction of the region of the optimum point.

The response surface allows inspecting, in a visual way, the response for certain area of the levels of the factors, allowing us to:

- Determine the combination of the factors levels that provides a good operative condition.
- Find the combination of levels that provides economic improvements.
- Investigate the mutual influence of the factors on the response variables, in analytic studies of fundamental processes.

Specifically, the response surface design is classified as a simultaneous method, being used in the stage of optimization. Their application allows selecting the optimum combination of levels, to obtain the best response for a specific condition [25].

The response y is described by a polynomial function of various independent variables x_i [25]:

$$y = f(x_i) + \varepsilon \qquad (1)$$

where ε represents the observed error in the response y.

The response surface design and the strategic analysis implied that the response variable (μ_y) is in function of the levels of quantitative factors represented by the variables $x_1, x_2, \ldots, x_k$. The polynomial models are used as practical approach to the real response function. The polynomial models commonly used for the analysis response surface are [18]:

- the lineal models of first order, applied to two factors:

$$\mu_y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 \qquad (2)$$

- the quadratic model, or of second order, for two factors:

$$\mu_y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 \qquad (3)$$

One approach to optimal performance is to vary one factor while keeping the other factors constant in order to get improved response with respect to the varied factor. This often does not bring about the effect of interaction of various parameters as compared to factorial design [23]. Response surface methodology is a useful model for studying the effect of several factors influencing the response by varying them simultaneously. The experimental design recently has been applied in the optimization of several processes [26–30].

The experiment design—response surface methodology is used in this work to optimize the reaction of C1 transformation into aromatic hydrocarbons (AH), using C2 as co-reactant and Zn-ZSM catalyst. The optimization is function of the following factors: X_1, reactions time (TOS); X_2, C2 space velocities (GHSV-C2); X_3, C1/(C1 + C2) molar fraction (XC1); X_4, reaction temperature. These factors were carefully selected based on our experience, taking into account the influence of the parameters in the reaction and the results showed in previous work [31]. The main objective of this study is to define the responses surfaces, finding the best combination in the reaction parameters in order to optimize the process, for that reason, the experiments design methodology was applied.

2. Experimental

2.1. Reaction conditions

The catalytic reactions of C1 + C2 were carried out in a fixed-bed continuous flow quartz reactor, with a 10 mm inner diameter and 20 cm length, at different reaction temperature over a Zn-ZSM-11 catalyst (Si/Al = 17; 2.5 wt% of Zn^{2+} as counter ion). The catalyst was added into the reactor designed to minimize homogeneous reactions. The catalyst particles were held on quartz wool plug, which was placed in the middle of the reactor. It was first degassed by blowing with N_2 at 600 °C for 2 h. Then, the bed temperature was adjusted to the required values with temperature controller. The furnace was a close-fitting, well-insulated stainless steel block, heated externally with high-temperature heater. This construction allows for effective heat transfer to the reactor wall, and provides isothermal operation of the reaction zone.

This reactor operated at atmospheric pressure, on-line, through automatic sampling, with a gas chromatograph equipped with a FID detector. Products were withdrawn periodically from the outlet of the reactor and analyzed by using a 2.2 m Porapak Q column. The delivery tubes were all heated to 210 °C at the exit of the reactor, to avoid liquid condensation in the pipework [16]. Replicate runs give a standard deviation in the methane and ethane conversion of 0.4–0.2 mol% C, respectively. The following reactants were used as feed: high purity methane (>99.97%) and ethane (>99.997%) supplied by AGA.

2.2. Factors

A Box–Behnken design was applied, the variables studied were: TOS, GHSV of ethane, molar fraction of C1/(C2 + C1) and reaction temperature. The following factors levels were used:

X_1 (TOS): 20, 40, 60 min.
X_2 (GHSV-C2): 810, 1525, 2240 ml/g h.
X_3 (C1 molar fraction): 0.4, 0.6, 0.8.
X_4 (reaction temperature): 520, 550, 580 °C.
Y_1 (response): C1 conversion (mol%).

The reasons of the levels chosen are:

TOS: the values of the TOS were taken up, as the conversion of C1 reached a minimum of 5% of conversion and the deactivation of the catalyst was not observed. Thus, 20, 40 and 60 min are selected as time on stream.
GHSV-C2: the values of the C2 space velocities are chosen according the previous report [32], where C2 alone generates reactive ad-species (ethyl carbenium ad-species, ethene, etc., and lower aromatic products), which can interact with C1 to activate it. Thus, the limits are 810, 1525, 2240 ml/g h.
C1 molar fraction: The C1/(C1 + C2) molar fractions are selected as a function of the C1 conversion. Above 0.8, the C1 is not activated, around 0.4, the C1 conversion is high but the highest conversion is about 0.8.
Reaction temperature: according the earlier results showed by us [15,32], the upper limit selected was 580 °C because at 600 °C, the ethane begins to convert in homogenous gas phase. The lowest limit is 520 °C according to C1 conversion, which is insignificant even in presence of C2 as co-reactant.

The natural variables (factors), TOS, GHVS-C2, XC1 and reaction temperature were codified for a better treatment of the data. This is a simple linear transformation of the original measurement scale for a factor; thus, the high value becomes +1 and the low value becomes −1. The codification was according to:

$$X_n = \frac{X - X_i}{\Delta X/2} \tag{4}$$

where X_1 = codified variable; X_i = central value; ΔX = step. The codification results are:

$$X_1 = \frac{TOS - 40}{40/2}, \quad X_2 = \frac{GHVSC_2 - 1525}{1430/2},$$

$$X_3 = \frac{XC_1 - 0,6}{0,4/2}, \quad X_4 = \frac{Temp - 550}{60/2}$$

2.3. Experimental design—response surface

In the response surface methodology (RSM), factorial designs are carried out, and the results are adjusted using mathematical models. These stages are known as displacement stage and design, respectively; these are repeated several times, screening the response surface obtained in the direction of the region of the best optimum point.

Table 1
Coded and decoded levels of the factors

Coded levels	X_1: TOS (min)	X_2: GHSV-C2 (ml/g h)	X_3: XC1	X_4: reaction temperature (°C)
(−1)	20	810	0.4	520
(+1)	60	2240	0.8	580
(0)	40	1525	0.6	550

In the most process, the relation between the response and the independent variables (factors) is ignored. Thus, the first step in the RSM consists in the determination of an appropriate approach to the real functional relation among, y and the group of independent variables. In general, a low order polynomial is used with some of the independent variables [18]. If the answer is described appropriately by a lineal function of the independent variables, the approach function is a first order model:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \varepsilon \tag{5}$$

When a curve exists in the system, a polynomial of superior order must be used, i.e., the second order model:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x1_2 + \beta_{22} x2_2 + \beta_{12} x_1 x_2 + \varepsilon \tag{6}$$

Then, the analysis of the response surface is made in terms of the adjusted surface. Such analysis will be approximately equivalent to the analysis of the real system, if the fitted surface is an appropriate approach to real response function.

A Box–Behnken design was applied in this study. The levels for TOS, GHSV-C2, XC1 and reaction temperature are shown in Table 1. The design, with the 27 experimental data, see Table 2, was analyzed by statistical soft: Statgraphics and Statistica.

3. Results and discussion

The Box–Behnken design, the coded and decoded levels of the factors and the response obtained are given in Table 2. Experiments were run in random order to minimize errors due to possible systematic trends in the variables. Some experiments were carried out in the central point, coded as "0", to estimate experimental error. Statistical analysis included the main effects and the interaction effects for the variable on the C1 conversion.

The analysis of variance (ANOVA) [24] partitions the variability of C1 conversion into separate pieces, for each of the effects. Then the ANOVA tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. The results obtained by the ANOVA test are shown in Table 3. In this case, three effects are significantly different from zero at the 95.0% confidence level (these p-values were highlighted as bold values, see Table 3). These factors are X_3 (XC1), X_4 (temperature) and the X_1–X_4 interactions (TOS–temperature). The R-squared statistic [18] indicates that the model explains 81.15% of the variability in C1 conversion. In this case, this value indicates that the model explains the 81% of the total variations. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of

Table 2
Box–Behnken design, containing the coded and decoded levels of the factors and the response

Run	Factors								Response
	Decoded				Coded				C1 conversion
	TOS	GHSV-C2	XC1	Temp.	X_1	X_2	X_3	X_4	
Box–Behnken design									
1	20	2240	0.6	550	−1	1	0	0	16.25
2	40	1525	0.8	580	0	0	1	1	11
3	40	1525	0.8	520	0	0	1	−1	1.4
4	60	810	0.6	550	1	−1	0	0	26.67
5	40	1525	0.6	550	0	0	0	0	21.78
6	20	810	0.6	550	−1	−1	0	0	17.64
7	40	1525	0.4	580	0	0	−1	1	29.1
8	40	1525	0.4	520	0	0	−1	−1	13.4
9	60	2240	0.6	550	1	1	0	0	16.6
10	60	1525	0.6	580	1	0	0	1	30.2
11	40	1525	0.6	550	0	0	0	0	20.3
12	40	810	0.8	550	0	−1	1	0	11.77
13	20	1525	0.6	580	−1	0	0	1	44.5
14	40	2240	0.4	550	0	1	−1	0	31.78
15	40	2240	0.8	550	0	1	1	0	1.7
16	20	1525	0.6	520	−1	0	0	−1	3.2
17	60	1525	0.6	520	1	0	0	−1	26.8
18	40	810	0.4	550	0	−1	−1	0	41.8
19	40	810	0.6	520	0	−1	0	−1	19
20	40	810	0.6	580	0	−1	0	1	35.6
21	60	1525	0.8	550	1	0	1	0	6.6
22	40	2240	0.6	580	0	1	0	1	37.9
23	60	1525	0.4	550	1	0	−1	0	36.68
24	40	1525	0.6	550	0	0	0	0	21
25	20	1525	0.8	550	−1	0	1	0	6.78
26	20	1525	0.4	550	−1	0	−1	0	36.84
27	40	2240	0.6	520	0	1	0	−1	18
Ascent									
28	40	1525	0.6	550	0	0	0	0	22.1
29	40.4	1489	0.55	550	0.02	−0.05	−0.25	0.18	25.0
30	39.8	1461	0.5	561	−0.01	−0.09	−0.5	0.36	29.4
31	39	1432	0.45	566	−0.05	−0.13	−0.75	0.55	35.2
32	37.4	1411	0.4	572	−0.13	−0.16	−1	0.75	42.1
33	35.2	1389	0.35	579	−0.24	−0.19	−1.25	0.97	40.2

independent variables, is 69.37%. *R*-squared adjusted value is also very high, which indicates a high significance of the model.

The appropriate hypothesis with respect to the effects of the treatment must be proven and an estimation of them must be realized. In order to prove the hypothesis, one assumes that the errors of the model are independent variables with normal distribution, average zero and variance σ^2. One assumes that variance is constant for all the levels of the factor [25]. Usually the verifi-

Table 3
Analysis of variance (ANOVA)

| Source of variation	Sum of squares	Df	Mean square	F-ratio	p-Value
X_1: A, factor A (TOS)	28.0296	1	28.0296	0.58	0.4570
X_2: B, factor B (GHSV-C2)	76.2558	1	76.2552	1.58	0.2267
X_3: C, factor C (XC1)	1883.76	1	1883.76	39.06	**0.0000**
X_4: D, factor D (temp.)	945.188	1	945.188	19.60	**0.0004**
X_1X_2 AB	18.8356	1	18.8356	0.39	0.5408
X_1X_3 AC	0.0001	1	0.0001	0.00	0.9989
X_1X_4 AD	359.103	1	359.103	7.45	**0.0149**
X_2X_3 BC	0.0006	1	0.0006	0.00	0.9972
X_2X_4 BD	2.7225	1	2.7225	0.06	0.8152
X_3X_4 CD	9.3025	1	9.3025	0.19	0.6664
Total error	771.729	16	48.233		
Total (corr.)	4094.93	26			
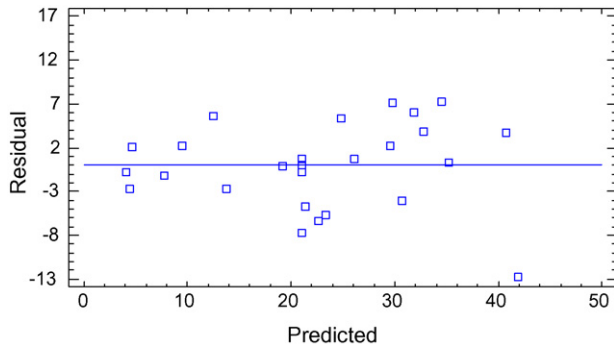
Fig. 1. Comparison of the predicted and observed residual value for C1 conversion.

cation of adjustment of the model consists to plot the residuals. If the model is correct and the suppositions are satisfied, the residuals neither must have any pattern, nor must be related to some other variable, including the response y. Thus, in a plot of the residuals versus the fit values y, no obvious pattern is revealed [25].

On the basis of the data showed in Fig. 1, the model is fairly good for predicting the C1 conversion. This figure confirms the superior prediction function of the model, and the feasibility of the statistical design of experiment method, to predict the critical process responses.

According to the data showed in Table 4, the following aspect can be underlined: the parameters that produce higher effect are X_3 (XC1 = −25), X_4 (temperature = 18) and the X_1–X_4 interactions (TOS–temperature = −19). The positive sign in the effect of the temperature means that the change from the lower to the higher level of the factor implies an increase in the response in 19 units. The negative signs in the effects, means that the change from the lower to the higher level, of the factor implies a decreasing in the response.

The model equation for the response surfaces fitted to the experimental data points, in coded unit, is as follows:

$$C1 \text{ conv.} = 21.6404 + 1.52833X_1 - 2.52083X_2 - 12.5292X_3$$
$$+ 8.875X_4 - 2.17X_1X_2 - 0.005X_1X_3$$
$$- 9.475X_1X_4 - 0.0125X_2X_3 + 0.825X_2X_4$$
$$- 1.525X_3X_4 \qquad (7)$$

Table 4
Estimated effects for the C_1 conversion

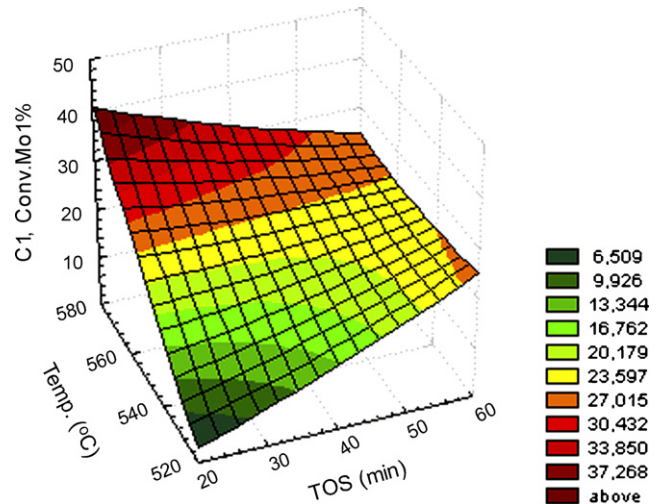| Factors	Effects
X_1 (TOS) A: factor A (TOS)	3.06
X_2 (GHSV-C2) B: factor B (GHSV-C2)	−5.04
X_3 (XC1) C: factor C (XC1)	**−25.06**
X_4 (temp.) D: factor D (temp.)	**17.75**
X_1X_2 AB	−4.34
X_1X_3 AC	−0.01
X_1X_4 AD	**−18.95**
X_2X_3 BC	−0.025
X_2X_4 BD	1.7
X_3X_4 CD	−3.05

Fig. 2. Response surface fitted for the design. C1 conversion as a function of TOS and reaction temperature.

According to the earlier experimental results and the data obtained by the design, it was necessary to carry out six new experiments with the purpose of finding an optimal area of operation to increase the C1 conversion. A path of steepest ascent for C1 conversion was explored from the center of the experimental region, along which the estimated response changes most quickly for the smallest change in the experimental factor (see Table 2 (Ascent)). The contours of estimated response surface products of this design are shown in Figs. 2–6. In order to a better interpretation of the surface, theses appear with the decoding values.

The statistic methodology applied in this work and the analysis of the factors and the figures, allow as suggesting the better operation conditions for this reaction. We propose the following as the optimal values for the variables:

- X_1 = TOS: 20–40 min.
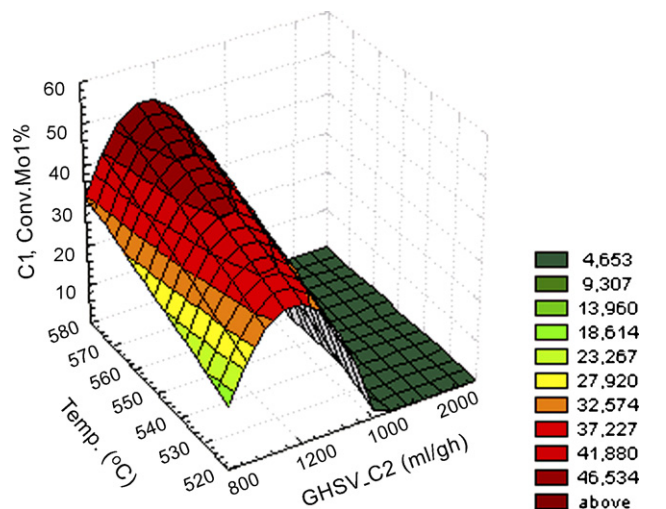- X_2 = GHSV-C2: 810–1200 ml/g h.

Fig. 3. Response surface fitted for the design. C1 conversion as a function of GHSV-C2 and reaction temperature variables.
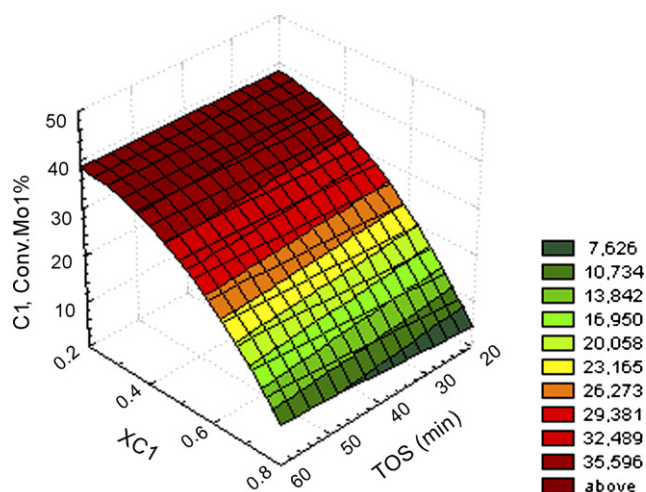
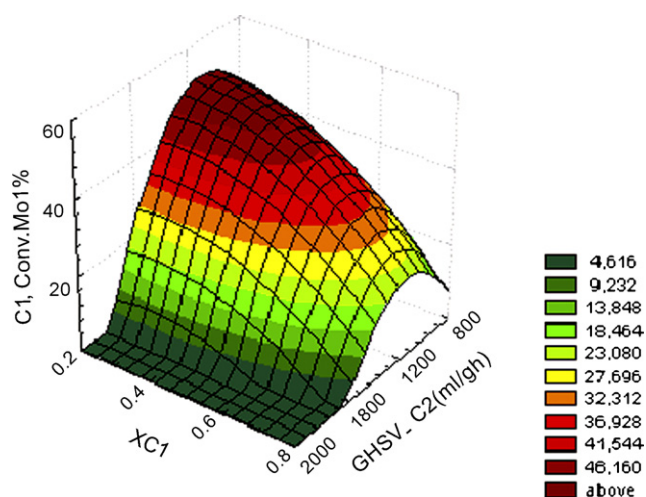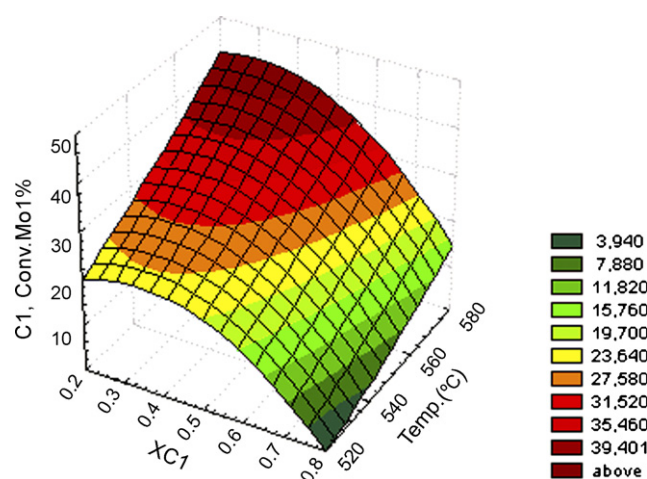Fig. 4. Response surface fitted for the design. C1 conversion as a function of TOS and XC1 variables.

Fig. 6. Response surface fitted for the design. C1 conversion as a function of XC1 and reaction temperature variables.

Fig. 5. Response surface fitted for the design. C1 conversion as a function of GHSV-C2 and XC1 variables.

- $X_3 = $ XC1: 0.2–0.4.
- $X_4 = $ reaction temperature: 550–580 °C.

In order to corroborate the statistic result, we carried out several reactions and the experimental data are shown in Table 5.

The results showed in Table 5 allow us to obtain the optimal values of the reaction conditions, based on statistic analyses.

With these data, we reach a higher C1 conversion (55 mol% C). It is interesting to mark that we arrive to these conclusions considering the influence of the separate variables and their main interactions.

In addition, according to the data indicated in Table 5, the C1 conversion increases with the temperature–TOS interaction. Nevertheless, based on previous results [15,32] to higher temperatures of reaction, such as 700 °C, the C2 only transforms in gas phase. At the same time when the TOS increases over the levels of the factors selected by us (for example, 100 min), the catalyst begins to deactivate itself more quickly, diminishing the conversion C1 and C2.

4. Conclusions

A design of experiment was carried out in order to optimize the C1 conversion. The statistic model applied in this work allowed us to interpret the overall process, considering the multivariate parameters. Applying the statistic methodology, the best operation conditions can be found. The highest C1 conversion (mol% C) was achieved working at these conditions. In the same way, the statistic methodology indicates that the following factors: XC1, the reaction temperature and the TOS–temperature interaction, have the higher effects.

From the catalytic point of view, and according to our previous results of C1 activation with C2 [15,32], the reaction

Table 5
C_1 Conversion in the optimal reaction conditions

Exp.	TOS (min)	GHSV-C2 (ml/g h)	XC1	Reaction temperature (°C)	C1 conversion (mol% C)
1	20	810	0.2	580	48.6
2	40	1200	0.2	580	50.5
3	40	810	0.4	550	50.0
4	20	810	0.4	580	50.4
5	20	1200	0.3	580	52.2
6	40	810	0.3	550	54.3
7	40	1200	0.3	580	55.4
8	40	810	0.3	580	56.1

mechanism seems to be a Rydeal type. Ethane is adsorbed onto the catalyst surface generating active ad-species, which are impacted from gas phase by C1. The reaction rate increases as the partial pressure of the gas phase species and the number of the chemisorbed ad-species increases, too. Thus, we suggest that this is the reason because at XC1 between 0.4–0.6 appears as the optimum partial pressure of C1, with sufficient quantities of C2 as ad-species, allowing their interaction.

Considering that the reaction takes place at a total pressure of 1 atm, the increase of XC1 up to 0.8, influences negatively in the amount of C2 ad-species, based on its low partial pressure. If the reaction temperature increases to 580 °C, C1 conversion increases, but at higher reaction temperature (700 °C), C2 and in minor proportion C1, reacting in gas phase. When the time on stream increases, within the values selected by us (i.e., 100 min), the catalyst begins to deactivate slowly, producing the diminution of C1 and C2 conversion. The Zn-species incorporated into catalyst are active because of its lower LUMO energy (low unoccupied molecular orbital), acting as new and strong Lewis acid sites, and allowing the chemisorption of active C2 ad-species, by the direct abstraction of a hydride producing a carbenium-like surface species through electron-donor–acceptor adduct (EDA) formation. Then, these species react in order to produce intermediates as C_3 and C_4 and more reactive olefins ($C_2=$, $C_4=$) and latter isoparaffin (i-C_4). The carbenium ad-species formed from them interact with C_1 producing its transformation to naphthenic and aromatics. It is interesting to observe, that the presence of strong Lewis sites (SLS) on the catalyst prevents the hydrogenation of intermediate alkenes, which would be efficiently introduced into polymerization, cyclization, dehydrogenation and aromatization complex mechanism. The statistic model applied in this work is a powerful tool to interpret the overall process from the multivariate parameters.

Acknowledgements

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