Research Article

Study of Syngas Conversion to Light Olefins by Response Surface Methodology

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The effect of adding MgO to a precipitated iron-cobalt-manganese based Fischer-Tropsch synthesis (FTS) catalyst was investigated via response surface methodology. The catalytic performance of the catalysts was examined in a fixed bed microreactor at a total pressure of 1–7 bar, temperature of 280–380°C, MgO content of 5–25% and using a syngas having a H₂ to CO ratio equal to 2. The dependence of the activity and product distribution on MgO content, temperature, and pressure was successfully correlated via full quadratic second-order polynomial equations. The statistical analysis and response surface demonstrations indicated that MgO significantly influences the CO conversion and chain growth probability as well as ethane, propane, propylene, butylene selectivity, and alkene/alkane ratio. A strong interaction between variables was also evidenced in some cases. The decreasing effect of pressure on alkene to alkane ratio is investigated through olefin readsorption effects and CO hydrogenation kinetics. Finally, a multiobjective optimization procedure was employed to calculate the best amount of MgO content in different reactor conditions.

1. Introduction

CO hydrogenation is an interesting catalytic reaction that converts the mixture of CO and H₂ called syngas into a wide spectrum of hydrocarbons. Light olefins are commercially desired products of CO hydrogenation reaction. Iron and cobalt are traditional catalysts and their modification has been investigated extensively. It has been reported that the use of bimetallic Fe-Co catalysts may enhance the olefin selectivity [1–3]. The papers have also reported that the addition of Mn to Fe or Co catalysts will cause a significant increase in light olefins formation and a decrease in methane selectivity [4–6]. Recently, a trimetallic Fe-Co-Mn catalyst for CO hydrogenation reaction has been developed and the effect of the preparation condition on the activity and selectivity to light olefins has been studied [7]. It was found that the catalyst calcined at 600°C for 6 h under air atmosphere has shown the best catalytic performance for CO hydrogenation.

To improve the CO hydrogenation reaction performance, the addition of structural promoters or supports into catalysts to suppress the agglomeration of active phases during time on stream and to improve the mechanical properties of catalysts

may be beneficial [8–10]. The choice of support for CO hydrogenation catalyst is dictated by several considerations including basicity, electronic modification, dispersion, and metal-support interactions. The primary laboratory studies indicated that structural promoters have a significant effect on the activity and selectivity of Fe-Co-Mn catalyst. Moreover, between four popular supports, SiO₂, TiO₂, Al₂O₃, and MgO, the later gives better selectivity to light olefins. So, it will be beneficial to closely investigate the effects of MgO on activity and selectivity of Fe-Co-Mn catalyst [11].

The selected approach for conducting an experimental work is important. The results of metal, promoter, and support effects and preparation condition on activity and selectivity of CO hydrogenation reaction have mainly emerged from one-variable-at-a-time experiments. These approaches are costly and time consuming. In addition, the interactions between the variables may not be investigated by traditional approaches. Several studies have been carried out in constant conditions while the catalyst performance may differ according to reactor conditions. For example, Dinse et al. have shown that the effect of Mn as a promoter on the activity and

selectivity of Co catalyst is dependent on the reactor pressure [11].

In recent years, design of experiments (DOE) and statistical tools has attracted researchers and several experimental studies have been conducted through DOE [12–18]. However, the application of DOE in CO hydrogenation reaction has been addressed only in some studies [16, 17].

As mentioned by Adesina [10], with a multitude of factors, there is a need for a statistically designed program for CO hydrogenation catalyst development both from the standpoint of runs minimization and information maximization and also the future CO hydrogenation catalyst design will benefit from the application of statistical tools in the formulation of a well-understood and predictive catalytic model. Having a variety of statistical tools, the response surface methodology is an efficient procedure in scientific studies. This methodology is a collection of statistical techniques for a designing of experiments, building the models, evaluating the effects of factors, and searching for the optimum conditions. The purpose of RSM is establishing the systematic modeling, demonstrating, and optimizing the behaviors via regression/statistical/graphical tools which lead to more efficient understanding of the complicated processes.

Although statistical methodologies and RSM have been used extensively in various scientific fields as well as catalysis science [12–15], a few studies for CO hydrogenation are based on statistical methodologies [16, 17] and no study has been conducted based on the response surface methodology.

While the major disadvantage of traditional one-variable-at-a-time techniques is that they do not include interaction effects among the variables, RSM demonstrates complete effects of the parameters on the process with minimum number of experiments.

The purpose of the present study is to investigate the effect of MgO as structural promoter on activity and product selectivity of CO hydrogenation reaction over Fe-Co-Mn catalyst through response surface methodology in different reactor conditions.

2. Experimental

The effect of support content and reactor condition on CO conversion and product distribution of CO hydrogenation has been studied. The catalyst used throughout the experiments consisted of a ternary mixture of Fe-Co-Mn which was prepared with the precipitation method. In the coprecipitation method, aqueous solutions of cobalt nitrate, iron nitrate and magnesium nitrate with similar molar ratios were premixed and the resulting solution heated to 70°C in a round-bottomed flask fitted with a condenser. Aqueous Na₂CO₃ was added to the mixed nitrate solution with stirring while the temperature was maintained at 70°C until optimized pH was achieved. The resulting precipitate was left in this medium for 2 h. The aged suspension was after that filtered, washed several times with warm distilled water until no further Na⁺ was observed in the washings tested by flame atomic absorption.

The precipitate was then dried in the oven (120°C, 16 h) to give a material denoted as the catalyst precursor, which was subsequently calcined in static air in the furnace (600°C, 6 h) to give the final catalyst. For preparation of the supported catalysts, the different amount (5, 15 and 25 wt%) of MgO support has been added separately to the mixed solution of iron and cobalt and magnesia nitrates

The effect of MgO content and operating conditions temperature and pressure was investigated by a second-order factorial design, the so-called Box Behnken design. The ranges of the variables were the following: temperature = 280–380°C; pressure = 1–7 bar; MgO = 5–25% wt.

Catalytic tests were carried out in a 1 cm diameter tubular fixed bed microreactor with a composite catalyst of 1 g. The catalyst was diluted with quartz wool for heat dissipation during CO hydrogenation process. The reaction tube was placed in a furnace equipped with temperature controller (JUMO IMAGO 500 Co.). Prior to the reaction, the catalysis was activated in situ using H₂ (30 mL/min) and N₂ (30 mL/min) gas mixture at 400°C for 2 hr. After reduction, purified H₂, CO, and N₂ gas were fed into the reactor. The flow rates of H₂, CO, and N₂ were controlled by three mass flow controllers (BROOKS 5850E). It was possible to divert the feed mixture entering or the products leaving the reactor to the GC for analysis. The feed and product gases were analyzed for CO and C hydrocarbons by an on-line GC model UNICAM Pro GC + (THERMO ONIX Co.).

The GC has three channels; hydrocarbon channel equipped with a capillary column type *CSAlumina* (length 30 m, diameter 0.53 mm), hydrogen channel consists of two packed column, *Haysep Q*, 60–80 mesh (length 1.5 m, diameter 0.125 in), and *MolSieve 5 A* (length 2 m, diameter 0.125), and permanent gases channel equipped with two columns, *Haysep QS*, 60–80 mesh (length 3 m, diameter 0.125), and *MolSieve 5 A* (length 2 m, diameter 0.125). The hydrogen and permanent channels are related to a TCD and hydrocarbon channel are contacted to an FID. The volume flow rate of H₂, CO, and N₂ and the ratio of H₂/CO were kept constant (30 mL/min, 15 mL/min, 30 mL/min, and 2, resp.) in all experiments.

Catalytic results are given in Table 1. The CO conversions, methane, ethane, propane, ethylene, and propylene selectivity are presented. In addition the chain growth probability factors were obtained by the following and are presented in the table:

$$\ln\left(\frac{W_n}{n}\right) = n \ln \alpha + \text{const}, \quad (1)$$

W_n : mole fraction of C_n hydrocarbons, n : number of hydrocarbons, and α Chain growth probability.

The mathematical relationship among the three variables and response was approximated by the second-order polynomial:

$$Y = B_0 + \sum_{i=1}^n B_i x_i + \sum_{ij} B_{ij} x_i x_j + \sum_{j=1}^n B_{jj} x_j^2, \quad (2)$$

Y : predicted response, x : test variables, and B : regression coefficient.

The test variables, in the model equation, are coded values according to the following:

$$x_i = \frac{X_i - X_i^*}{\Delta X_i}, \quad (3)$$

where x_i is the coded value of the i th independent variable, X_i is the uncoded value of the i th independent variable, X_i^* is the uncoded value of the i th independent variable at the center point and, ΔX_i is the step change value.

Predicted responses (Y) are CO conversion, CH_4 , C_2H_4 , C_3H_6 , C_2H_6 , C_3H_8 , alkene/alkane ratio, and chain growth probability.

The student's t -test was used to determine the significance of the regression coefficients of the parameters. The P values were used as a tool to check the significance of each interaction among the variables. The larger the value of T (and smaller the value of P), the more significant is the corresponding coefficient term. Finally an analysis of variance (ANOVA) was carried out for a further check of the model adequacy. All regressions/statistical analysis were conducted with MINITAB software.

3. Results and Discussion

On the basis of preliminary experiments and RSM, the effect of temperature, pressure, and MgO content on CO conversion, methane, ethane, propane, ethylene, propylene and butylene selectivity as well as alkene/alkane (O/P) ratio, and chain growth probability was studied. A three-factor three-coded level Box-Behnken design was used to determine the responses dependency to the variables. The application of RSM yielded the regression equations for each variable according to the temperature, pressure, and MgO content.

The significance of each coefficient was determined by F value and P value and the statistically important terms are presented in Table 2. Then the full quadratic regression models were pruned by stepwise elimination of statistically unimportant terms. The analysis of variance (ANOVA) table was employed to test the statistical significance of the ratio of mean square due to regression and mean square due to residual error. A summary of the ANOVA is also given in Table 2. Generally, P values lower than 0.05 indicate that the model is considered to be statistically significant at the 95% confidence level. The ANOVA of quadratic regression models demonstrates that all models are highly significant as it is evident from Fisher's F -test value with a low probability value. For example, the results indicate that the full quadratic model of methane is statistically significant at 96.6% confidence level. The goodness of the fit of the model was tested by determination coefficient (R^2). The value of adjusted determination coefficient R_{adj}^2 is also high to advocate high significance of the models.

3.1. CO Conversion. According to the statistical analysis (Table 2), MgO content, temperature, pressure, and their quadratic terms statistically have significant effect on CO conversion. The interaction between MgO content with temperature and pressure are also statistically significant. The

only insignificant term is $T \times P$. The pruned response surface model of CO conversion is as follows:

$$\begin{aligned} X_{\text{CO}} = & 28.033 - 12.657\text{MgO} + 5.431T + 8.441P \\ & - 10.813\text{MgO}^2 + 5.265T^2 + 6.095P^2 \\ & - 3.485\text{MgO} \times T - 4.635\text{MgO} \times P. \end{aligned} \quad (4)$$

Surface plots of the CO conversions have been given in Figure 1. Temperature and pressure have an increasing effect on CO conversion, but in high MgO content, the increasing effect of pressure and temperature has been changed. Both surface plots and regression coefficients indicate that the MgO content has a more significant effect than pressure and temperature. CO conversion increases to a maximum level and then decreases when MgO content increases. The increasing effect of MgO on CO conversion may be attributed to its important effect on surface area of catalyst. The BET results (Table 3) have indicated that MgO increases the surface area, so the chance of reactant adsorption increases and higher values of CO conversion are observed. However, higher surface area may enhance the metal-supports interaction that suppresses the reducibility of the metals. So, as evidenced in response surface plots, the higher CO conversions in optimum amount of MgO are observed.

3.2. CH_4 Selectivity. The variation of CH_4 selectivity with content of MgO and reaction conditions is shown as surface plots in Figure 2. CH_4 selectivity generally shows an increasing trend with an increase in reactor pressure especially in moderate to high MgO content. On the other hand, temperature has an increasing effect in low to moderate MgO contents. It is evident from response plots that MgO has strong interaction with temperature and pressure in complete agreement with statistical results of Table 1 that shows $\text{MgO} \times T$ and $\text{MgO} \times P$ terms are statistically significant. The pruned RSM model of CH_4 selectivity can be presented by the following equations:

$$\begin{aligned} S_{\text{CH}_4} = & 52.586 + 0.675\text{MgO} + 1.35T + 2.925P \\ & + 3.414T^2 + 3.5\text{MgO} \times P. \end{aligned} \quad (5)$$

3.3. Ethane and Propane Selectivity. The change in ethane and propane selectivity with content of MgO and operating conditions (temperature and pressure) plotted as surface curves is shown in Figure 3. It is observed that C_2H_6 selectivity increases with the increase of temperature and pressure while it decreases with the increase in content of MgO. Statistical analysis shows that all variables (T , P , MgO) are important. In addition, the quadratic terms for MgO and temperature are statistically significant. Surface plots for propane in Figure 3 show that propane selectivity increases with the increase in pressure especially in low to moderate MgO content. According to the statistical analysis, temperature has no important effect on the propane selectivity; however, its interaction with MgO is significant (Table 2). The pruned

TABLE 1: Experimental design based on Box Behnken, catalyst: precipitated equimolar Fe-Co-Mn- $x\%$ MgO, x : 5, 15, 25% wt, and total flow rate: 75 mL/min, $H_2/CO = 2$.

Point	Variables				Responses							
	MgO	Temp	P	%CO	S_{CH_4}	$S_{C_2H_6}$	$S_{C_2H_4}$	$S_{C_3H_8}$	$S_{C_3H_6}$	$S_{C_4H_8}$	O/P	alpha
1	5	380	4	44.1	58.7	12.3	12.1	3.5	11.6	1.8	0.65	0.31
2	25	330	1	5.9	44.5	2.1	27.5	1.4	24.4	0.1	2.10	0.44
3	25	280	4	7.84	58.8	7.2	13.4	1.0	19.4	0.2	1.01	0.41
4	25	380	4	13.5	57.7	10.1	11.9	2.7	16.2	1.5	0.91	0.40
5	25	330	7	13.73	57.0	9.1	12.3	2.9	17.8	0.9	0.86	0.35
6	15	330	4	28.8	54.4	7.4	14.8	2.7	19.5	1.3	1.11	0.38
7	15	330	4	27.3	53.3	8.2	14.4	3.1	18.7	2.4	1.11	0.39
8	15	330	4	28	54.4	6.4	15.7	2.7	19.3	1.5	1.13	0.38
9	5	330	1	23.63	53.0	5.4	28.2	1.1	12.2	0.0	1.41	0.29
10	15	380	1	34.85	52.8	5.3	24.7	0.9	16.1	0.1	1.37	0.33
11	15	280	1	27.27	52.7	1.7	23.7	1.0	20.9	0.0	1.63	0.37
12	5	330	7	50	51.5	13.4	11.5	5.6	15.3	2.7	0.90	0.39
13	5	280	4	24.5	49.4	10.4	15.1	4.9	18.8	2.5	1.05	0.42
14	15	280	7	42.42	57.7	12.2	8.3	4.6	15.4	1.9	0.69	0.36
15	15	380	7	53.03	60.2	11.8	7.9	4.0	14.1	2.1	0.61	0.33

TABLE 2: Results of response surface methodology for different responses.

Response surface model	Statistical significant terms			Statistical criterions					
	Simple	Quadratic	Interaction	Complete RSM model		F regression (P value)	Pruned RSM model		
				R^2	R^2_{adj}		R^2	R^2_{adj}	F regression (P value)
CO conversion	all	all	$MgO \times P$ $MgO \times T$	99.6	98.8	124.72 (0.000)	99.5	98.8	143.23 (0.000)
CH_4 selectivity	P	$T * T$	$MgO \times P$ $MgO \times T$	91.2	75.3	5.73 (0.034)	74.6	60.6	5.30 (0.015)
C_2H_6 selectivity	T, P MgO	$MgO * MgO$ $T * T$	—	98.3	95.3	32.7 (0.001)	93.7	90.2	26.50 (0.000)
C_2H_4 selectivity	P	$T * T$ $P * P$	—	99.2	97.9	73.35 (0.000)	98.4	97.7	152.99 (0.000)
C_3H_8 selectivity	MgO P	—	$MgO \times P$ $MgO \times T$	97.1	91.8	18.36 (0.003)	95.8	93.5	41.38 (0.000)
C_3H_6 selectivity	MgO T	—	$MgO \times P$	90	72.1	5.02 (0.045)	76.3	66.9	8.06 (0.004)
C_4H_8 selectivity	MgO P	$P * P$	—	94	83.1	8.64 (0.014)	78.3	72.4	13.24 (0.001)
O/P ratio	T, P MgO	$T * T$ $P * P$	$MgO \times P$	98.8	96.6	45.02 (0.000)	97.4	95.4	49.06 (0.000)
Chain growth probability, α	MgO T	$P * P$	$MgO \times P$ $MgO \times T$	97.4	92.7	20.61 (0.002)	93	87.7	17.83 (0.000)

FIGURE 1: CO conversions according to the MgO content and reactor conditions. MgO has a decreasing effect on CO conversion in high pressures. In low pressure, the CO conversion approaches to a maximum as MgO increases.

FIGURE 2: Effect of temperature, pressure, and structural promoter on the methane selectivity. MgO has changed the CH_4 selectivity dependency of temperature and pressure. The pressure increases the selectivity when MgO is high. Temperature has an increasing effect on methane selectivity especially in low MgO content.

FIGURE 3: Effect of temperature, pressure, and structural promoter on the propane and ethane selectivity. MgO decreases the ethane and propane selectivity and pressure increases the selectivity.

response surface models of C_2H_6 and C_3H_8 selectivity are as follows:

$$S_{C_2H_6} = 6.692 - 1.625MgO + 1.0T + 4.0P + 1.288MgO^2 + 1.538T^2 \quad (6)$$

$$S_{C_3H_8} = 2.807 - 0.888MgO - 0.05T + 1.588P + 0.775MgO \times T - 0.75MgO \times P. \quad (7)$$

3.4. Alkene Selectivity. The variations in C_2H_4 , C_3H_6 , and C_4H_8 selectivity with content of MgO, pressure, and temperature of reaction are shown as surface plots in Figure 4. According to the surface plots, it is observed that with the increase of pressure, C_2H_4 and C_3H_6 selectivity decreases while C_4H_8 selectivity increases. Temperature has no statistically significant effect on C_2H_4 and C_4H_8 selectivity while its decreasing effect on C_3H_6 selectivity is important. The response plots also show that the C_3H_6 selectivity increases with increasing MgO content. In addition, the MgO and temperature dependency of C_3H_6 selectivity depends on the reactor pressure. The pruned fitted second-order alkene

selectivity model in three factors for Box Behnken-coded data is given by

$$S_{C_2H_4} = 15.546 - 0.488T - 8.013P - 2.856T^2 + 3.894P^2 \quad (8)$$

$$S_{C_3H_6} = 17.313 + 2.487MgO - 2.062T - 1.375P - 2.425MgO \times P \quad (9)$$

$$S_{C_4H_8} = 1.6 - 0.538MgO + 0.925P - 0.625P^2. \quad (10)$$

3.5. Alkenes to Alkanes Ratio. It is appeared from statistical analysis results of Table 2 that all variables have important effect on alkene/alkane (O/P) ratio. The quadratic terms of temperature and pressure are also statistically significant. In addition, the interaction between MgO and pressure is important.

FIGURE 4: Effect of temperature, pressure, and structural promoter on ethane, propene, and butylenes selectivity, MgO increases the propene selectivity, and pressure decreases the propene selectivity while increases the butylenes selectivity.

TABLE 3: Effect of MgO loading on BET results of catalyst.

MgO support loading	Fresh calcined		
	SSA (m ² /g)	PV (cm ³ /g)	PS (Å)
5 wt%	91.54	1.23×10^{-2}	23.33
10 wt%	99.22	1.15×10^{-2}	23.00
15 wt%	103.49	1.63×10^{-2}	23.41
20 wt%	97.57	1.49×10^{-2}	24.21
25 wt%	93.49	1.27×10^{-2}	22.07

SSA: specific surface area; PV: pore volume; PS: pore size.

The pruned response surface model of O/P is

$$\frac{O}{P} = 1.126 + 0.109\text{MgO} - 0.105T - 0.431P - 0.228T^2 + 0.182P^2 - 0.183\text{MgO} \times P. \quad (11)$$

Response surface plots (Figure 5) indicate that O/P decreases with the increase in pressure. The O/P ratio increases to a maximum and then decreases as temperature

increases. The plots also indicate that MgO has a positive effect on O/P only in low pressures. In high pressures the MgO has a negative effect.

3.6. Chain Growth Probability. The results of Table 2 indicate that MgO content, temperature, and pressure have a statistically important effect on chain growth probability. In addition, the interaction between temperature and MgO and also pressure and MgO is important.

FIGURE 5: Effect of temperature, pressure, and structural promoter on Alkene to alkane ratio; MgO increases the O/P ratio in low pressures. O/P approaches to a maximum as temperature increases. Pressure decreases O/P .

The pruned fitted second-order chain growth probability model in three factors for Box Behnken-coded data is given by

$$\begin{aligned} \alpha = & 0.38457 + 0.02513\text{MgO} - 0.02288T - 0.00025P \\ & - 0.02632P^2 + 0.02525\text{MgO} \times T - 0.4650\text{MgO} \times P. \end{aligned} \quad (12)$$

Figure 6 shows the 3D response surface plot for the chain growth probability. The surface plots indicate that the chain growth probability approaches to a maximum with increasing pressure. The MgO content generally increases the chain growth probability in low to moderate pressures. Figure 6 also exhibits the response arising from the interaction between MgO, temperature, and pressure.

3.7. Investigation of Alkene Readsorption Effects. The results of the previous sections indicate that pressure decreases the alkene selectivity (O/P ratio). Alkenes are primary products of CO hydrogenation reaction. However, several researchers have shown that alkenes may get readsorbed on the catalyst

surface and mainly reincorporated or hydrogenated into paraffins [18, 19]. In many studies, the deviations from ideal ASF theory are attributed to this phenomenon [18, 19]. Figure 7 shows ASF plots of design points. Some points follow the ASF curves; however, deviations are observed for many points especially in high pressures. A statistical analysis of R^2 as a measure of deviation from ASF curves according to the pressure, MgO, and temperature may clearly show that R^2 values decrease as pressure increases; however, the results have not been presented here. So, it may be concluded that the chance of alkene readsorption/hydrogenation increases with the increase of pressure.

On the other hand, all R^2 values are above 0.88 (see Figure 7) that shows the deviations from ASF theory may not be too severe. So, the decreasing effect of pressure on the O/P may not be completely attributed to the alkene readsorption effects. In our previous kinetic study [20], we showed that the rate of CH_4 and alkane formation on bimetallic Fe-Co catalyst is proportional to $P_{\text{H}_2}^3$ and P_{CO} , while the rate of alkene formation is proportional to $P_{\text{H}_2}^2$ and P_{CO} . Recent studies indicate that the mechanism of the reaction and kinetic rates

FIGURE 6: Effect of temperature, pressure, and structural promoter on chain growth probability, α . α approaches to a maximum as pressure increases. MgO increases α in low to moderate pressures.

TABLE 4: Optimum conditions according to the nonlinear programming approach.

Type of optimization	Goal	Global solution			Predicted responses	
		MgO	T	P	X_{CO}	O/P
1	Single objective	5	380	7	63.98	—
2	Maximization of O/P	24.26	284.29	1.00	—	1.90
3	Two objectives	22.11	288.10	1.000	16.38	1.87
4		16.44	352.09	1.00	27.18	1.67
5		16.44	371.34	1.00	31.36	1.50
6		11.88	379.07	1.00	37.86	1.26
7		5.00	325.65	7.00	48.25	0.97

on Fe-Co may not change by addition of Mn [21]. So, the kinetic rates clearly indicate that the increase of pressure in high H_2/CO ratio kinetically decreases the O/P ratio.

The effect of MgO on O/P ratio is interesting. The MgO increases the O/P especially in low and moderate pressures. The statistical analysis also indicates that MgO has an improving effect on O/P. While, MgO has no statistically important effect on C_2H_4 selectivity, It has improving effect on C_3H_6 selectivity (see Figure 4). The effect of MgO on surface area and pore structure of catalyst are presented in Table 3. The BET results show that surface area and pore volume of catalysts increase as MgO content increases. The increase of surface area and pore volume may enhance the alkene readsorption and reduces the O/P. However, the opposite results have been evidenced here. So, as mentioned in the previous paragraph a mechanism other than alkene readsorption may cause this.

3.8. Searching the Optimum Conditions. A nonlinear programming approach through desirability function was employed to obtain the optimal conditions for different objectives. The results are presented in Table 4. The objectives are maximization of CO conversions and/or O/P ratio.

The maximum of CO conversion is achieved in high temperature and pressure (380°C and 7 bar) and low MgO content, while the maximum O/P ratio is occurred in low pressures (1 bar) and nearly low temperatures (284°C) and moderate MgO content (24%). The results of Table 4 also indicate that to maximize both CO conversion and O/P ratio, the pressure must be kept in low limit (1 bar). In this condition, high values of O/P ratio (1.87) are obtained only in maximum CO conversion 16%. The higher values of CO conversions (27%, 31% and 37%) are obtained with the increase of temperature (351, 371, 379°C, resp.), but the decrease in O/P ratio occurred (1.67, 1.5, 1.26, resp.). In

FIGURE 7: Continued.

FIGURE 7: Distribution of products according to the ASF theory.

addition, the MgO content must change (16, 16, and 11.44, resp.). The optimization results also indicate that the higher value of CO conversion (up to 50%) is obtained in high pressure (7 bar). To achieve the highest possible value of O/P (0.97) in this condition, the temperature and MgO must be 325°C and 5%, respectively.

4. Conclusions

The structural promoters or supports are usually added into catalysts to improve the CO hydrogenation performance. They are able to suppress the agglomeration/sintering of active phases during time on stream and to improve the mechanical properties of catalyst through enhancement of the catalyst's surface area and pore structure. However, it is evidenced here that structural promoters may significantly affect the activity and selectivity of catalyst as indicated in other literature. The application of RSM yielded the regression equations for CO conversion, methane, ethane, propane,

ethylene, propylene, and butylenes selectivity as well as chain growth probability and O/P according to the temperature, pressure, and MgO content. Our study through statistical tools showed that CO conversion increases up to a maximum and then decreases significantly as MgO content increases. In addition, the response surface models clearly demonstrate the changes of selectivity according to the MgO content, reaction temperature, and pressure. The results indicated that MgO content significantly alters the dependency of methane to the temperature and pressure. In addition, MgO has a positive effect on the propylene selectivity in moderate to low pressures. The RSM indicated that MgO is able to affect the O/P and chain growth probability and its effect depends on the temperature and pressure. A multiobjective optimization based on desirability function was proposed to search the best conditions of temperature, pressure, and also MgO content. The optimization results showed that to maximize both CO conversion and O/P , the MgO content must change according to the reactor conditions.

Nomenclature

R^2 :	Correlation coefficient
R^2_{adj} :	Adjusted correlation coefficient
S:	Selectivity
T:	Value of Student's <i>t</i> -test
V:	Volume flow rates (mL/min)
X_{CO} :	CO conversion
x_i :	Coded value of the <i>i</i> th independent variable
X_i :	Uncoded value of the <i>i</i> th independent variable
X_i^* :	Uncoded value of the <i>i</i> th independent variable at the center point
ΔX_i :	Step change value
Y:	Predicted response.

Abbreviation

ASF:	Anderson Schults Flory
RSM:	Response surface methodology
ANOVA:	Analysis of variance.

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