Effects of Process Factors on Carbon Dioxide Reforming of Methane over Ni/SBA-15 Catalyst

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The process of CO_2 reformation of CH_4 was conducted over a 5% Ni/SBA-15 catalyst under various experimental conditions. Operating temperature (600-750 °C), gas hourly space velocity (4000-12000 hr^{-1}), and CO_2/CH_4 feed molar ratio (0.67-1.50) were selected as independent parameters (factors). Process performances were evaluated as conversions of CH_4 (21.1-79.6%) and CO_2 (42.4-98.7%) as well as H_2/CO product molar ratio (0.573-0.992). All process performances were enhanced at higher levels of temperature and low values of gas velocity. An increase in feed molar ratio has determined a significant increase in CH_4 conversion and a slighter decrease in CO_2 conversion and H_2/CO molar ratio. A statistical model based on a 2^3 factorial plan was used to predict the process performances depending on its factors.

Keywords: methane reforming, carbon dioxide, Ni/SBA-15, factorial experiment, syngas

The process of carbon dioxide reforming of methane ($CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$), also known as dry reforming of methane (DRM), has a high potential to convert two major greenhouse gases, *i.e.*, CH_4 and CO_2, into synthesis gas (syngas). DRM is commonly accompanied by reverse-water-gas-shift (RWGS) reaction ($CO_2 + H_2 \leftrightarrow CO + H_2O$) as well as by Bouduard reaction ($2CO \leftrightarrow C + CO_2$) and CH_4 cracking ($CH_4 \leftrightarrow C + 2H_2$) leading to formation of coke (C) [1-10]. Unlike the syngas obtained by steam reforming ($CH_4 + H_2O \leftrightarrow CO + 3H_2$) and partial oxidation of methane ($CH_4 + 1/2O_2 \leftrightarrow CO + 2H_2$), that produced by DRM has a low H_2/CO molar ratio and it is suitable for obtaining oxygenated chemicals (*e.g.*, methanol, formaldehyde, dimethyl ether) and higher hydrocarbons via Fischer-Tropsch synthesis [1-9,11,12].

DRM process is thermodynamically favoured at very high temperatures (>700 °C) resulting in a high consumption of energy [1,10]. Noble (Ru, Rh, Pt, Pd, Ir) or transitional (Ni, Co) metals dispersed onto various supports (commonly Al_2O_3, La_2O_3, MgO, CaO, TiO_2, SiO_2, CeO_2, ZrO_2) are generally used for obtaining a high yield of syngas at lower temperatures [1,2,4,6-13].

Ni-based catalysts are widely used due to their availability, lower cost, and catalytic performance comparable to that of noble metals [1-4,6,8-10,12,13]. A major drawback of Ni catalysts is their rapid deactivation owing to C deposition. To develop supported Ni catalysts with high activity and resistance to C formation, the following strategies have been commonly applied [1-9,12,13]: (i) using a high surface area support (mesoporous molecular sieves, activated carbon, carbon nanotubes); (ii) selecting a suitable catalyst preparation method (precipitation, sol-gel, plasma treatment); (iii) introducing a second active metal (Ru, Rh, Pt, Co); (iv) adding a promoter (alkaline earth metals, Cu, V, Sm, La).

The support nature can heavily influence the performance of supported catalysts. Supported Ni catalysts based on mesoporous molecular sieves (*e.g.*, SBA-15, SBA-16, MCM-41) have demonstrated superior stability and activity [1,2,6,7,9,13]. SBA-15 and SBA-16 are extensively used as catalyst supports due to their high surface area (usually larger than 700 m²/g), superior thermal stability, and ordered pore structure [1,2,6,7,9,11,13,14].

A study on the effect of process factors, including reaction temperature, pressure, feed molar ratio, and gas hourly space velocity (GHSV), on reactant conversion, product selectivity, and catalyst stability is essential for designing, operating, optimizing, and scaling-up the DRM process. RWGS reaction is enhanced by higher pressures [8,15], consequently DMR process is usually conducted under atmospheric pressure. A high temperature can avoid side reactions, *i.e.*, RWGS, Bouduard, and CH_4 cracking, but it implies more energy [1].

Conversions of CH_4 and CO_2 increase with an increase in operating temperature as effect of endothermic nature ($\Delta H_{298} = +247$ kJ/mol) of DMR reaction [1-10,12,13]. Typically, H_2/CO syngas molar ratio is less than 1 due to RWGS reaction leading to an extra consumption of H_2 and an extra production of CO [7]. Moreover, H_2/CO ratio generally increases towards unity with the process temperature [1,3,5,7-10,12,13,16]. Higher values of GHSV, *i.e.*, lower values of residence time, results in lower levels of reactant conversion and H_2/CO syngas molar ratio [4,5]. An increase in CO_2/CH_4 feed molar ratio commonly determines an increase in CH_4 conversion as well as a decrease in CO_2 conversion and H_2/CO syngas molar ratio [1,3,5,10,17].

This paper has aimed at studying the process of CO_2 reforming of CH_4 over a Ni/SBA-15 catalyst. The effects of process factors, *i.e.*, operating temperature, GHSV, and CO_2/CH_4 feed molar ratio, on its responses in terms of reactant conversion and H_2/CO syngas molar ratio were evaluated.

Experimental part

SBA-15 support preparation

SBA-15 support was prepared according to the procedure described in the related literature [2,6,7,11,14]. Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) copolymer (Pluronic P123, PEG_{20} PPG_{70} PEG_{20}, Merck) was used as template agent and tetraethyl orthosilicate (TEOS, Merck) as silica source. Pluronic P123 (4 g) was dissolved in a 2 M HCl solution (160 mL) under stirring at room temperature for 30 min and then TEOS (6.4 g) was added. The mixture was stirred at room temperature for 24 h and further aged at 90 °C for another 24 h. The suspension was filtrated, washed with

distilled water, and dried in an oven at 60 °C for 24 h. The dried solid was further calcined at 500 ° C for 5 h in order to remove the template agent, cooled to room temperature, and then ground into a powder.

Ni/SBA-15 supported catalyst preparation

5% Ni/SBA-15 supported catalyst was synthesized by wet impregnation method using nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, Merck) as a nickel source [7,14]. SBA-15 powder (10 g) and a solution (10 mL) of $Ni(NO_3)_2 \cdot 6H_2O$ (0.2476 g) were mixed in a sonicator at room temperature for 30 min. The suspension was filtrated and dried in an oven at 60 °C for 24 h. The dried catalyst was further calcined at 300 °C for 30 min and then reduced under H_2/Ar (5% H_2) at 500 °C for 1 h.

Catalytic tests

DRM process was performed in a fixed bed quartz tubular reactor under atmospheric pressure. Supported catalyst (1 cm^3) was placed between two layers of quartz wool in the centre of tubular reactor. Process temperature was measured by a thermocouple located in the centre of catalyst bed.

Prior to the reforming process, the supported catalyst was reduced *in situ* at 700 °C for 2 h under pure H_2 (Linde) flow (20 mL/min). Then, N_2 (Messer) was fed in the system for 1 hr in order to remove any residual H_2 in the reactor. After that, catalytic tests were conducted using a feed gas mixture consisting of CH_4 (Messer) and CO_2 (Messer). The effluent was analyzed using a Shimadzu gas chromatograph (Shimadzu Corporation) equipped with a thermal conductivity detector (TCD).

Experimental tests were conducted for various levels of each process factor, *i.e.*, operating temperature (t=600-750 °C), GHSV (v=4000-12000 h^{-1}), and CO_2/CH_4 feed molar ratio (R_F=0.67-1.50). Process performances were expressed in terms of CH_4 and CO_2 conversions as well as of H_2/CO product molar ratio.

Results and discussions
Experimental data

17 experimental runs were performed under various operating conditions. The levels of process factors corresponding to each run (exp.) are summarized in table 1.

Table 1
LEVELS OF PROCESS FACTORS

Exp.	t (°C)	v (hr^{-1})	R_F	Exp.	t (°C)	v (hr^{-1})	R_F
1	600	6000	1	8	750	6000	1.50
2	650	6000	1	9	750	6000	0.67
3	700	6000	1	10	700	8000	1
4	750	6000	1	11	700	6000	1.50
5	750	4000	1	12	700	8000	1.50
6	750	8000	1	13	750	8000	1.50
7	750	12000	1	14-17	725	7000	1.25

The effect of operating temperature (t=600-750 °C) on the conversions of CH_4 (C_A) and CO_2 (C_B) as well as on H_2/CO product molar ratio (R_P) for v=6000 h^{-1} and R_F=1 (exp. 1-4 in table 1) is highlighted in figure 1. Depicted results emphasize an increase in reactant conversions (C_A=21.1-56.8% and C_B=42.4-93.2%) and H_2/CO molar ratio (R_P=0.573-0.896) with the temperature, according to the data reported in the literature [1-10,12,13,16]. Subunit values of R_P and supraunit ones of C_B/C_A ratio (1.6-2) indicate the presence of RWGS reaction. It is also noted

that each process performance can be predicted well (R^2>0.980) by a straight line.

The influence of GHSV (v=4000-12000 h^{-1}) on the process performances in terms of C_A, C_B, and R_P for t=750 °C and R_F=1 (exp. 4-7 in table 1) is revealed in figure 2. According to other findings [4,5], an increase in v has determined a decrease in C_A (35.9-65.5%), C_B (67.9-98.7%), and R_P (0.667-0.992) due to a shorter contact time between the reactants and catalyst. On the other hand, a low level of GHSV causes a faster deactivation of the catalyst as an effect of C deposition [5]. Accordingly, under these experimental conditions, the optimal range of GHSV is 6000-8000 h^{-1}. Moreover, the results presented in figure 2 emphasize that the process performances can be predicted very well ($R^2 \geq 0.991$) by straight lines.
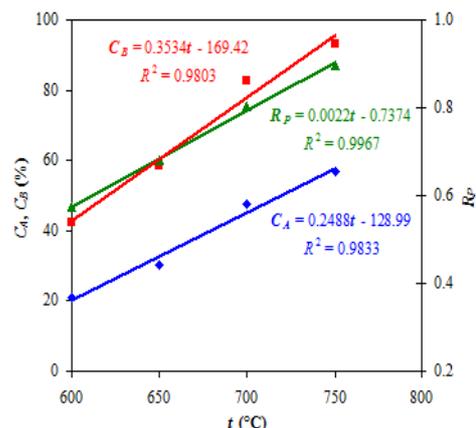
Fig. 1. Effect of operating temperature on CH_4 (A) and CO_2 (B) conversions and H_2/CO molar ratio (v=6000 hr^{-1}, R_F=1).
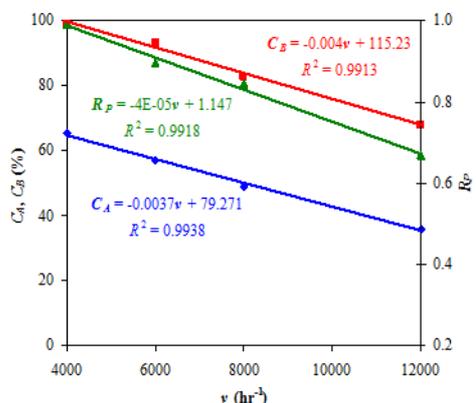
Fig. 2. Effect of GHSV on CH_4 (A) and CO_2 (B) conversions and H_2/CO molar ratio (t=750 °C, R_F=1)

The results depicted in figure 3, *i.e.*, reactant conversions and H_2/CO product molar ratio *vs.* CO_2/CH_4 feed molar ratio (R_F=0.67-1.50) for t=750 °C and v=6000 h^{-1} (exp. 4, 8, and 9 in table 1), highlight a significant increase in C_A (from 44.4% to 79.6%), a slight decrease in C_B (from 96.1% to 89.3%), and a very slight decrease in R_P (from 0.905 to 0.883) with an increase in R_F, as reported by other researchers [1,3,5,10,17]. Taking into account the conversion of CH_4 (C_A), under the experimental conditions considered in these runs, the optimal range of CO_2/CH_4 feed molar ratio is 1-1.50. It is also noticed that each process performance can be predicted very well (R^2>0.997) by a straight line.

Prediction of process performances

A statistical model based on a 2^3 factorial plan was used to predict the process performances in terms of C_A, C_B, and R_P. 2 levels of each process factor were selected within the optimal ranges, *i.e.*: t=700, 750 °C, v=6000, 8000 h^{-1}, and
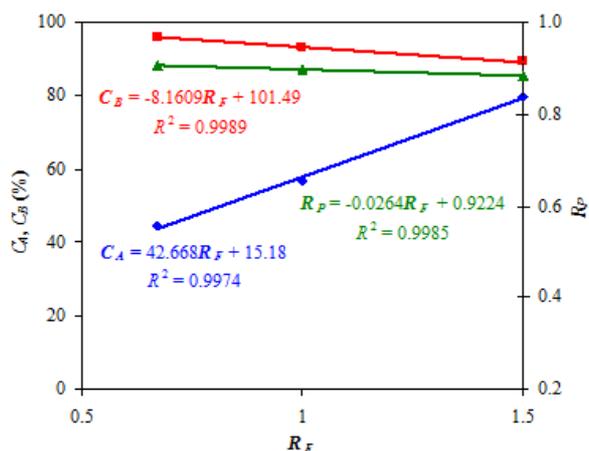
Fig. 3. Effect of feed molar ratio on CH_4 (A) and CO_2 (B) conversions and H_2/CO molar ratio
(t=750 °C, v=6000 h⁻¹)

In the figure:
$C_B = -8.1609 R_F + 101.49$
$R^2 = 0.9989$

$R_P = -0.0264 R_F + 0.9224$
$R^2 = 0.9985$

$C_A = 42.668 R_F + 15.18$
$R^2 = 0.9974$

R_F=1, 1.50. Dimensionless values of process factors are given by eqs. (1)-(3), where t_{cp}=725 °C, v_{cp}=7000 h⁻¹, and R_F=1.25 are centre-points. Process factors and performances corresponding to 8 experimental runs (exp. 3, 4, 6, 8, 10-13 in table 1) are summarized in table 2 (no. 1-8).

$$x_1 = \frac{t - 725}{25} \quad (1)$$

$$x_2 = \frac{v - 7000}{1000} \quad (2)$$

$$x_3 = \frac{R - 1.25}{0.25} \quad (3)$$

Regression coefficients of statistical model described by eq. (4), i.e., β_{ij} (i=1..N=8, j=1..3), which are presented in table 3, were determined by processing the data given in table 2 (no. 1-8) according to characteristic procedure of a 2^3 factorial experiment.

$$y_j = \beta_{1j} + \beta_{2j} x_1 + \beta_{3j} x_2 + \beta_{4j} x_3 + \beta_{5j} x_1 x_2 + \\ + \beta_{6j} x_1 x_3 + \beta_{7j} x_2 x_3 + \beta_{8j} x_1 x_2 x_3 \quad (4)$$

In order to determine the significance of regression coefficients using the Student's test [18-20], 4 centre-point runs (N_{cp}=4) were performed (exp. 14-17 in tables 1 and 2). Characteristic parameters of centre-point runs, i.e., mean value of response ($y_{j,mn,cp}$), reproducibility standard deviation ($\sigma_{rp,j}$), and number of degrees of freedom (v_1), as well as standard deviation associated to regression coefficients ($\sigma_{\beta,j}$) and values of Student's random variable (t_{ij}), given by eqs. (5)-(9), are presented in table 3.

$$y_{j,mn,cp} = \frac{\sum_{k=1}^{N_{cp}} y_{jk,cp}}{N_{cp}} \quad (5)$$

No.	Exp.	t (°C)	v (hr⁻¹)	R_F	x_1	x_2	x_3	C_A (%)	C_B (%)	R_P
1	3	700	6000	1	-1	-1	-1	47.6	82.6	0.805
2	4	750	6000	1	1	-1	-1	56.8	93.2	0.896
3	10	700	8000	1	-1	1	-1	40.8	74.9	0.714
4	6	750	8000	1	1	1	-1	48.7	82.4	0.845
5	11	700	6000	1.50	-1	-1	1	66.3	81.1	0.715
6	8	750	6000	1.50	1	-1	1	79.6	89.3	0.883
7	12	700	8000	1.50	-1	1	1	56.8	70.3	0.697
8	13	750	8000	1.50	1	1	1	68.2	77.3	0.838
9	14	725	7000	1.25	0	0	0	58.9	82.5	0.804
10	15	725	7000	1.25	0	0	0	58.5	83.1	0.814
11	16	725	7000	1.25	0	0	0	55.7	81.2	0.785
12	17	725	7000	1.25	0	0	0	57.3	80.6	0.775

Table 2
EXPERIMENTATION MATRIX FOR 2^3 FACTORIAL EXPERIMENT

	i	1	2	3	4	5	6	7	8
	β_{i1} (%)	58.10	5.225	-4.475	9.625	-0.400	0.950	-0.750	-0.075
	$y_{1,mn,cp}$ (%)	57.6							
j=1	$\sigma_{rp,1}$ (%)	1.438							
	$\sigma_{\beta,1}$ (%)	0.508							
	t_{i1}	114.3	10.28	8.804	18.94	0.787	1.869	1.476	0.148
	t_{i1}-3.176	>0	>0	>0	>0	<0	<0	<0	<0
	β_{i2} (%)	81.39	4.163	-5.162	-1.888	-0.538	-0.363	0.537	0.238
	$y_{2,mn,cp}$ (%)	81.85							
j=2	$\sigma_{rp,2}$ (%)	1.150							
	$\sigma_{\beta,2}$ (%)	0.407							
	t_{i2}	200.1	10.23	12.69	4.641	1.322	0.891	1.322	0.584
	t_{i2}-3.176	>0	>0	>0	>0	<0	<0	<0	<0
	β_{i3}	0.799	0.066	-0.026	-0.016	0.002	0.011	0.010	-0.008
	$y_{3,mn,cp}$	0.795							
j=3	$\sigma_{rp,3}$	0.018							
	$\sigma_{\beta,3}$	0.006							
	t_{i3}	127.6	10.60	4.092	2.535	0.260	1.737	1.577	1.338
	t_{i3}-3.176	>0	>0	>0	<0	<0	<0	<0	<0

Table 3
SIGNIFICANCE OF REGRESSION COEFFICIENTS OF EQ. (4)

$$\sigma_{rp,j} = \sqrt{\frac{\sum_{k=1}^{N_{cp}}\left(y_{jk,cp} - y_{j,mn,cp}\right)^2}{\upsilon_1}} \qquad (6)$$

$$\upsilon_1 = N_{cp} - 1 = 3 \qquad (7)$$

$$\sigma_{\beta,j} = \frac{\sigma_{rp,j}}{\sqrt{N}} \qquad (8)$$

$$t_{ij} = \frac{|\beta_{ij}|}{\sigma_{\beta,j}} \qquad (9)$$

Regression coefficients satisfying the condition $t_{ij} - t_{\alpha,\upsilon_1} > 0$ were considered as significant, where $t_{\alpha,\upsilon_1} = 3.176$ represents the theoretical value of Student's variable corresponding to a significance level (α) of 0.05 and $\upsilon_1 = 3$ [20]. Considering only significant coefficients (bold characters in table 3), the statistical model described by eq. (4) becomes:

$$y_1 = C_A = 58.10 + 5.225x_1 - 4.475x_2 + 9.625x_3 \qquad (10)$$

$$y_2 = C_B = 81.39 + 4.163x_1 - 5.162x_2 - 1.888x_3 \qquad (11)$$

$$y_3 = R_P = 0.799 + 0.066x_1 - 0.026x_2 \qquad (12)$$

Regression equations (10)-(12) reveal the following issues: (i) CH_4 conversion (C_A) increases with operating temperature (x_1) and CO_2/CH_4 feed molar ratio (x_3) as well as decreases with an increase in GHSV (x_2), the effect of x_3 being more significant; (ii) CO_2 conversion (C_B) increases with x_1 and decreases with an increase in x_2 and x_3, the influence of x_3 being less significant; (iii) H_2/CO molar ratio increases with x_1, decreases with an increase in x_2, and is invariant with x_3; moreover, the effect of x_1 is more important than that of x_2. Statistical model described by eqs. (10)-(12) could be applied to estimate the performances of DMR process for factor levels within the ranges considered in the statistical analysis, i.e., t=700-750 °C, v=6000-8000 h^{-1}, and R_F=1, 1.50.

Conclusions

DRM process was studied over a 5% Ni/SBA-15 catalyst under different conditions. The effects of process factors, i.e., operating temperature (t=600-750 °C), GHSV (v=4000-12000 h^{-1}), and CO_2/CH_4 (B/A) feed molar ratio (R_F=0.67-1.50) on its performances in terms of reactant conversions (C_A=21.1-79.6% and C_B=42.4-98.7%) and H_2/CO product molar ratio (R_P=0.573-0.992) were evaluated.

All process performances exhibited a linear increase with t (v=6000 hr^{-1}, R_F=1) and a linear decrease with v (t=750°C, R_F=1). CH_4 conversion increased linearly, whereas CO_2 conversion and H_2/CO molar ratio decreased linearly with R_F (t=750 °C, v=6000 h^{-1}). Moreover, the effect of R_F on C_A was more significant than that on C_B and R_P. Optimal (o) ranges of process factors were selected as follows: t_o=700-750 °C, v_o=6000-8000 h^{-1}, and R_{Fo}=1-1.50. A 2^3 factorial design was used to obtain regression equations between the process performances and its factors within the optimal ranges. All process performances were invariant with the interactions between the factors.

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