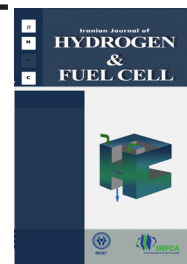


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Optimization of the preparation procedure of Ni/Al₂O₃ catalyst for steam reforming of n-butane

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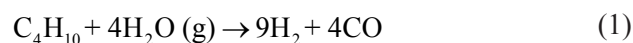
Abstract

Performance of Ni/Al₂O₃ catalysts (10 wt.% Ni) in steam reforming of n-butane was investigated in terms of n-butane conversion, selectivity to hydrogen, and hydrogen yield. The catalysts were prepared by the precipitation-sedimentation method at different precipitation, drying and calcination temperatures as well as precursors. Synthesized catalysts were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and BET analyses. Mathematical predictive formulas were generated for responses by Design Expert software. Also, the optimum condition of the catalyst preparation was obtained by using the response surface methodology (RSM). Ultimately, it was concluded that Ni- Nitrate as the precursor was the most favorable and the overall optimum condition were: $T_{\text{precipitation}} = 30^{\circ}\text{C}$, $T_{\text{drying}} = 115^{\circ}\text{C}$, and $T_{\text{calcination}} = 700^{\circ}\text{C}$.

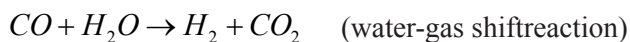
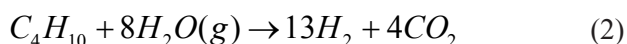
1. Introduction

Hydrogen is of particular interest as a future clean fuel for both combustion engines and fuel cells [1]. Although fossil fuels are unrenewable, they will be the most economic source of hydrogen until 2050 [2]. Among feedstocks, n-Butane holds a special position because of its abundant in Iran. Steam reforming (SR) and partial oxidation (POX) are two important methods for syngas production [3], in

which hydrocarbons are used as the feedstock. Steam reforming is an endothermic catalytic process that could be suppressed by coke formation. However, the presence of steam may decrease carbon deposition on the active sites of the catalyst. In steam reforming of n-butane, the H₂/CO ratio is more than 3, according to the following reactions:



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Various catalysts have been used in steam reforming. However, Ni-based catalysts are more common in industrial applications due to their lower price and the greater availability of nickel compared to other noble metals [4, 5]. Moreover, the performances of Ni-based catalysts are comparable with those based on more expensive noble metals [6, 7]. To find a proper Ni-based catalyst for steam reforming processes a range of different considerations, such as the effect of additives [4, 8], type of support [9], and nickel content [1, 10], on the final catalytic performance of catalysts have been taken into account. In addition some other effective parameters, such as the type of nickel precursors [11, 12] and the synthesis temperatures [3, 13], for different catalysts have been individually investigated.

The optimal designs are usually applied in occasions involved in irregular experimental regions, a nonstandard model, and unusual sample size requirements and the obtained coefficients from this method are very accurate [14].

Final properties of a catalyst depends on preparation method and its parameters. Among them precipitation, drying and calcination temperatures as well as precursors are more important, but haven't been investigated in previous studies. Therefore, in the present study these parameters were optimized by response surface methodology (RSM). In this way, the optimal regions of the aforementioned parameters were determined based on the response surfaces of n-butane conversion, selectivity to hydrogen and yield of hydrogen, separately.

2. Material and methods

2.1. Catalyst preparation

The γ - Al_2O_3 was prepared by the precipitation method. In detail, 1M solutions of Aluminum Nitrate ($Al(NO_3)_3 \cdot 9H_2O$, Merck, extra pure) as well as sodium carbonate (Na_2CO_3 , Merck, extra pure) were prepared as the aluminum source and precipitating agent, respectively. The Aluminum Nitrate solution was added drop wise at a rate of 1 mL/min to a vessel containing 200 mL deionized water at a temperature of 70 °C while being stirred at 850 rpm. The sodium carbonate solution was also added to adjust the pH to around 7. After the precipitation, the vessel content was aged for 30 min at a stirring rate of 300 rpm. The precipitate was then filtered and washed several times with deionized water in order to eliminate impurities. Finally, the product was dried at 110 °C for 12 h with a ramp of 1°C/min, followed by calcination in air at 600 °C for 4 h with a ramp of 6°C/min.

The Ni/ γ - Al_2O_3 catalysts (10 wt.% Ni) were prepared by the precipitation-sedimentation method, in which two types of raw materials, i.e. $Ni(NO_3)_2 \cdot 6H_2O$ and $Ni(CH_3COO)_2 \cdot 4H_2O$, were used. First, 7.2 g γ - Al_2O_3 was suspended in 500 mL deionized water at a stirring rate of 850 rpm. Then, 1 M solutions of Nickel Nitrate and sodium carbonate were added dropwise. The sodium carbonate solution was used to adjust the pH to around 7. Once the precipitation was finished, the solution was aged for 30 min at a stirring rate of 300 rpm. The precipitate was then filtered and washed several times with deionized water. Finally, the product was dried for 12 h and calcined in air for 4 h in which the drying and calcination ramp rates were 1 and 6°C/min, respectively. This process was repeated in different precipitation, drying and calcination temperatures as well as with a Nickel Acetate precursor in order to investigate their effects on the steam reforming of n-butane. It should be mentioned that the range of precipitation, drying and calcination temperatures in the catalyst preparation processes were 30- 80, 90- 140 and 600- 800°C, respectively. The variables investigated in this study are provided in Table 1.

Table 1. Selected parameters and their values for designing the experiments.

Factor	Low level (-1)	High level (+1)	Center point (0)	Unit
A = T _{precipitation}	30	80	55	°C
B = T _{drying}	90	140	115	°C
C = T _{calcination}	600	800	700	°C
D = P _{recursor}	Ni-Nitrate	Ni-Acetate	-	-

2.2 Catalyst characterization

The XRD analysis was performed by a Philips PW3040/60 diffractometer with Cu monochromatic radiation ($\lambda = 1.5456 \text{ \AA}$). SEM images were taken by a scanning electron microscope (TESCAN-Vega series) and the BET surface areas of catalysts were determined by nitrogen adsorption using a CHEMBET-3000 system (Quantachrome Instruments). It should be mentioned that the 2- theta was between 10- 110°, step size of 2- theta was 0.02° and scan step time was 0.35 s.

2.3 Catalytic tests

Figure 1 shows the experimental set-up used for the steam reforming of n-butane. Catalytic performance tests were carried out in a stainless steel fixed bed reactor (I.D. 10 mm) located in a furnace capable of heating to 1200°C and equipped with a PID controller. In each experiment, 1 g of catalyst (grain size of 297-595 μm) was charged into the reactor. Prior to the main reaction, the catalysts were reduced by H_2 . After reduction, a feed gas mixture of steam and n-butane was entered to the reactor. The n-butane (higher than 99%) was supplied by Mahan Gas Company. After

process stabilization, the product stream was analyzed on line using a gas chromatograph (manufactured by Agilent Company) equipped with a sample loop and a thermal conductivity detector. To measure the amount of products, two GC columns called a Molecular Sieve (for hydrogen and carbon monoxide) and a Plot-Q (for other products) were used.

Feed Conversion, Selectivity to H_2 and Hydrogen Yield were calculated by the following formulas:

Conversion of *n* – butane (%) =

$$\frac{C_{(n-C_4H_{10})in} - C_{(n-C_4H_{10})out}}{C_{(n-C_4H_{10})in}} \times 100\% \quad (1)$$

Selectivity to hydrogen (%) =

$$\frac{C_{(H_2)out}}{C_{(H_2)out} + C_{(CO_2)out} + C_{(CO)out}} \times 100\% \quad (2)$$

Hydrogen Yield = Conversion of *n*butane
× Selectivity to Hydrogen

(3)

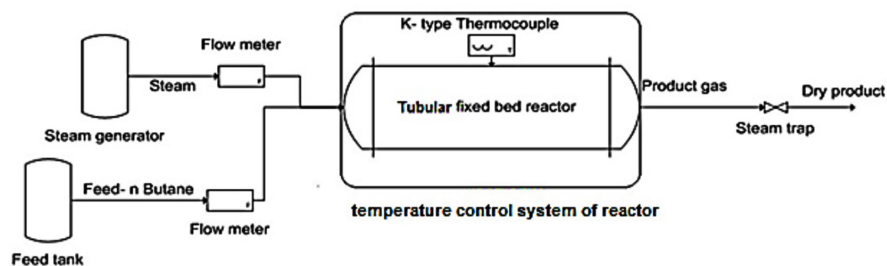


Fig. 1. Experimental set-up used for steam reforming of n-butane.

3. Results and discussion

3.1. Catalytic performance

The parameters investigated in this study are provided in Table 1. Accordingly, 19 experiments were considered by Design Expert v.7.0.0 and using a standard RSM design called D-optimal design, in order to investigate the significance of parameters as well as their interaction effects. The lower and upper limits of the parameters were also chosen based on previous studies [1, 4, 11, 13, 16-19]. Results are summarized in Table 2.

3.2. Characterization of the catalysts

Because of the large number of catalysts, typically two catalysts prepared by different precursors were characterized. XRD patterns of these synthesized catalysts are shown in Figure 2. As seen, an alloy of NiO and Al_2O_3 ($\text{NiO}.\text{Al}_2\text{O}_3$) has been formed.

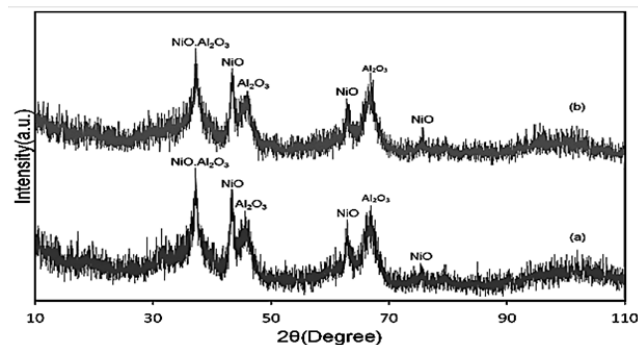


Fig. 2. XRD patterns of synthesized catalysts: (a) Catalyst produced by using Ni-Nitrate precursor: run No. 6, and (b) Catalyst produced by using Ni-Acetate precursor: run No. 17.

Scherrer equation is an equation to calculate mean size of particles: $\tau = \frac{K\lambda}{\beta \cos \theta}$.

Where τ is the mean size of the crystalline domains, and β is the line broadening at half of the maximum intensity peak called FWHM. In Figure 2 amounts of β for samples No. 6 (nitrate as precursor) and No. 17 (acetate as precursor) are 0.48 and 0.63, respectively.

Table 2. Results of experiments in various conditions.

Run	T _{precipitation} (°C)	T _{drying} (°C)	T _{calcination} (°C)	Precursor	Conversion (%)	Selectivity (%)	Yield × 10 ⁺²
1	50	121	600	Nitrate	82.65	67.66	55.92099
2	80	90	800	Nitrate	80.09	65.17	52.19465
3	30	140	800	Nitrate	69.74	61.16	42.65298
4	30	90	640	Acetate	81.81	53.66	43.89925
5	60	140	690	Nitrate	83.89	66.83	56.06369
6	70	118	800	Nitrate	80.27	70.23	56.37362
7	30	90	600	Nitrate	75.71	62.65	47.43232
8	30	90	800	Nitrate	75.44	60.96	45.98822
9	54	90	600	Acetate	67.82	42.55	28.85741
10	30	110	630	Acetate	89.52	75.68	67.74874
11	48	118	800	Acetate	54.39	33.54	18.24241
12	30	140	600	Acetate	61.90	53.06	32.84414
13	72	90	750	Acetate	69.64	45.24	31.50514
14	77	90	800	Acetate	82.09	63.23	51.90551
15	58	95	660	Nitrate	85.58	69.85	59.77763
16	80	90	600	Nitrate	86.57	64.17	55.55197
17	80	140	800	Acetate	88.48	75.22	66.55466
18	80	140	600	Nitrate	79.41	64.07	50.87799
19	70	123	700	Acetate	87.27	71.15	62.09261

This reveals that particles of the catalyst resulting from the nitrate precursor are bigger than those of the catalyst resulting from the acetate precursor. It can be concluded that dispersion of NiO in the catalyst resulting from the acetate precursor is better than that of the catalyst resulting from the nitrate precursor.

SEM images of the selected samples are also shown in Figure 3. These images confirm the formation of nanosize particles. As seen, different precursors lead to dissimilar morphologies. In other words, the catalyst resulting from the Ni-Acetate precursor reveals a fibrous structure while the catalyst resulting from Ni-Nitrate causes a spherical morphology.

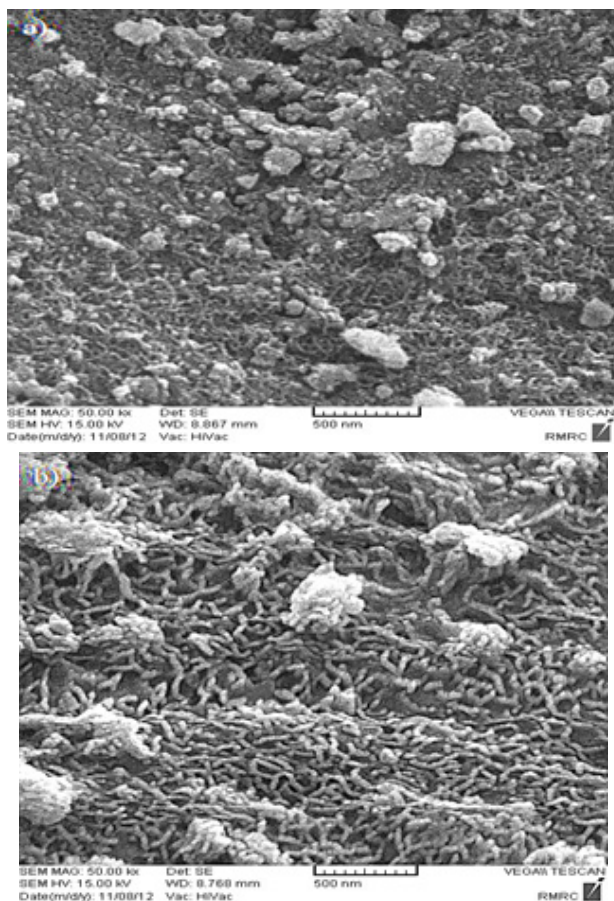


Fig. 3. SEM images of two synthesized catalyst: (a) Catalyst produced by using the Ni-Nitrate precursor: run No. 6, and (b) Catalyst produced by using the Ni-Acetate precursor: run No. 17.

3.3 Numerical study of process parameters

A numerical study helps finding optimum conditions to maximize objective functions. In catalysis, three parameters are important to maximize: conversion, selectivity and yield. However, yield is not independent from the other parameters. In this study, we tried to investigate each parameter separately. To show the results clearly, the models were converted to figures using Matlab software.

3.3.1 Analysis of variance of n-butane conversion

Analysis of Variance (ANOVA) of n-butane conversion was performed and the results are given in Table 3. The relationship between the response and input factors was expressed by the following model, in which the factors were entered in coded values:

$$X(\%) = 88.24 + 7.09 A + 4.54 B - 4.68 C - 7.19 D + 8.49 AC + 3.29 AD + 5.51 BC + 3.79 BD - 3.29 CD - 12.78 B^2 - 11.31 C^2 - 4.74 ABC + 14.85 ACD + 5.23 BCD - 8.72 A^2B$$

To transform an actual value to coded value, the following equation should be used:

$$\text{Coded value} = \frac{l - l_0}{\Delta l}$$

In which, l is the actual value, l_0 is the null point and Δl is the factor's range from null point to the end.

A, B and C are the coded values of precipitation, drying and calcination temperatures, respectively, and D is the categorical factor where (-1) is Ni-Nitrate and (+1) is Ni-Acetate. The p-value is 0.0017, which indicates the model is significant. The ANOVA results demonstrate that the precursor as well as precipitation temperature are the most effective parameters to maximize n-butane conversion. Moreover, the interaction between precipitation and calcination temperatures (AC) is the most effective interactional effect.

Table 3. ANOVA table of n-butane conversion.

Source	Sum of Squares	df	Mean Square	F-Value	p-value Prob > F
Model	1668.70	15	111.25	89.59	0.0017
A ($T_{\text{precipitation}}$)	264.95	1	264.95	213.38	0.0007
B (T_{drying})	38.86	1	38.86	31.29	0.0113
C ($T_{\text{calcination}}$)	130.69	1	130.69	105.24	0.0020
D (Precursor)	358.42	1	358.42	288.65	0.0004
AC	295.58	1	295.58	238.04	0.0006
AD	61.21	1	61.21	49.29	0.0059
BC	264.16	1	264.16	212.73	0.0007
BD	82.16	1	82.16	66.16	0.0039
CD	64.23	1	64.23	51.73	0.0055
B ²	299.94	1	299.94	241.55	0.0006
C ²	271.89	1	271.89	218.96	0.0007
ABC	77.19	1	77.19	62.16	0.0043
ACD	589.35	1	589.35	474.62	0.0002
BCD	242.42	1	242.42	195.23	0.0008
A ² B	101.34	1	101.34	81.61	0.0029
Residual	3.73	3	1.24		
Total	1672.42	18			

In order to validate and test the obtained model, two samples were synthesized at base levels of effective factors (-1) and zero levels with $D = -1$; at the base levels of the factors the model predicted the response 75.56% and at zero levels 95.43% while the response was 78% and 92% in experimental tests, respectively. Therefore, it is concluded that the prediction is acceptable.

Figure 4 indicates the response of the model versus the effective parameters.

Figure 4a shows results obtained by using Ni-Nitrate as the precursor. This figure demonstrates that the maximum conversion is obtained at the maximum precipitation temperature and at moderate level amounts of drying and calcination temperatures. Therefore to maximize the conversion, the optimum conditions are the following, approximately:

$$T_{\text{precipitation}} = 80^{\circ}\text{C} \quad (A=+1), \quad T_{\text{drying}} = 115^{\circ}\text{C} \quad (B=0), \\ T_{\text{calcination}} = 700^{\circ}\text{C} \quad (C=0)$$

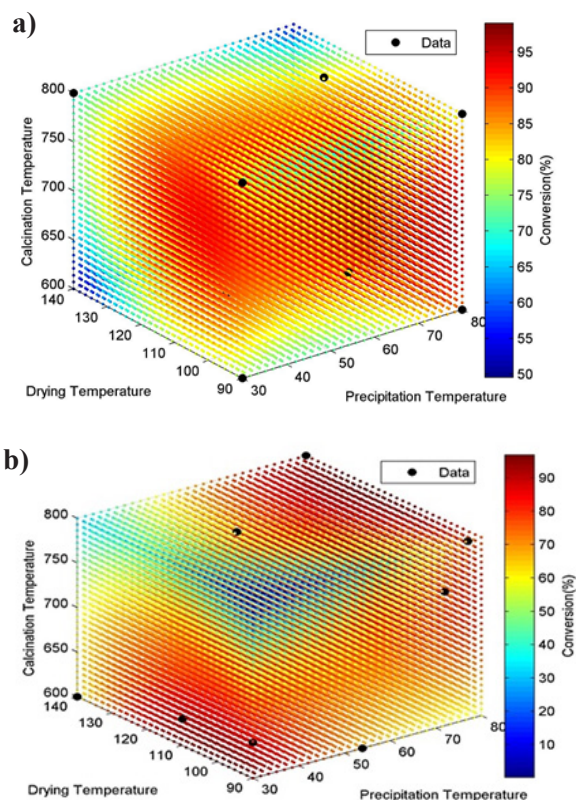


Fig. 4. The response surface of the data for conversion of n-butane with the catalyst using a) Ni-Nitrate as the precursor and b) Ni-Acetate as the precursor.

Figures 4b shows the results obtained by using Ni-Acetate as the precursor. This figure indicates that the maximum conversion is obtained when the drying temperature is at a moderate level and the precipitation and calcination temperatures are their highest values. Therefore, optimum conditions are the following, approximately:

$$T_{\text{precipitation}} = 80^{\circ}\text{C} (A=+1), T_{\text{drying}} = 115^{\circ}\text{C} (B=0) \text{ and } T_{\text{calcination}} = 800^{\circ}\text{C} (C=+1)$$

In summary, results of optimization indicated that Ni-Acetate is a more appropriate precursor than Ni-Nitrate to maximize the conversion.

3.3.2 Analysis of variance of hydrogen selectivity

The ANOVA results of hydrogen selectivity are given in Table 4. The relationship between the response and input factors was expressed by the following model, in which the factors were entered in coded values:

$$\begin{aligned} \text{Selectivity (\%)} = & 72.03 + 8.08 A + 6.65 B - 4.82 C \\ & - 10.04 D + 12.45 AC + 6.12 AD + 3.74 BC + 6.05 BD \\ & - 5.35 CD - 18.09 B^2 - 8.25 C^2 - 7.66 ABC + 19.43 ACD \\ & + 3.18 BCD - 8.06 A^2B \end{aligned}$$

As mentioned, A, B and C are the coded values of precipitation, drying and calcination temperatures, respectively, and D is the categorical factor where (-1) is Ni-Nitrate and (+1) is Ni-Acetate. The p-value is 0.0283, which indicates the model is significant. According to the results the precursor is the most effective parameter. In addition, the precipitation and calcination temperatures as well as their interaction have a considerable effect on H_2 selectivity.

To validate and test the obtained model, two catalysts were synthesized at base levels (-1) and zero levels of effective parameters with $D = -1$; at the base levels of the factors the model predicted the response 61.94% and at zero levels 82.07% while the response was 63% and 75% in experimental tests, respectively. Therefore, it is concluded that the prediction is acceptable.

Figure 5 indicates response of the model versus the

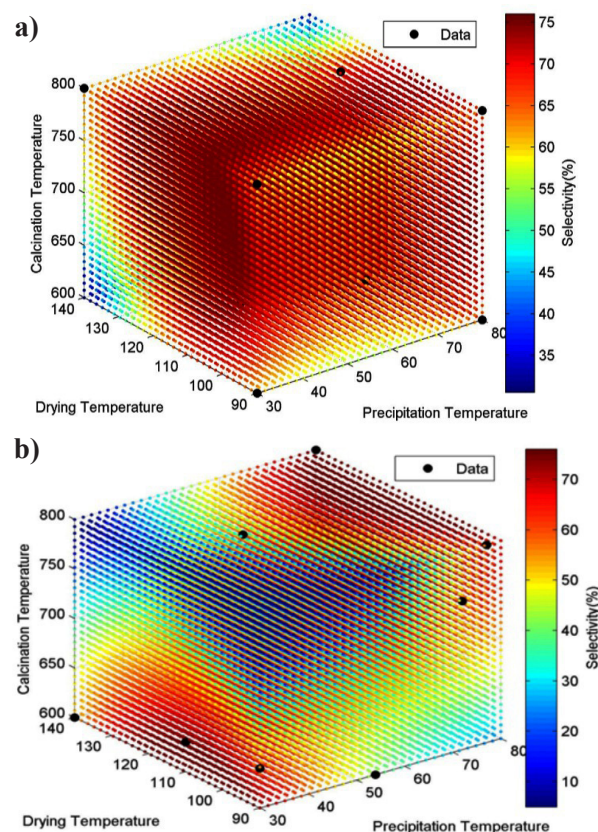


Fig. 5. The response surface of the data for H_2 selectivity with the catalyst using a) Ni-Nitrate as the precursor and b) Ni-Acetate as the precursor.

effective parameters.

Figures 5a shows the results obtained by using Ni-Nitrate as the precursor. This figure demonstrates that the maximum H_2 selectivity is obtained at high levels of precipitation and calcination temperatures and a low level of drying temperature. Therefore, to maximize the H_2 selectivity, the optimum conditions are the following, approximately:

$$T_{\text{precipitation}} = 80^{\circ}\text{C} (A=+1), T_{\text{drying}} = 100^{\circ}\text{C} (B=-0.6), T_{\text{calcination}} = 800^{\circ}\text{C} (C=+1)$$

Figures 5b shows the results obtained by using Ni-Acetate as the precursor. This figure indicates that the maximum selectivity is obtained at a moderate drying temperature and high precipitation and calcination temperatures. Therefore, optimum conditions are the following, approximately:

Table 4. ANOVA table of H₂ selectivity in steam reforming of n-butane.

Source	Sum of Squares	df	Mean Square	F-Value	p-value Prob > F
Model	2226.52	15	148.43	13.07	0.0283
A (T _{precipitation})	344.50	1	344.50	30.34	0.0118
B (T _{drying})	83.35	1	83.35	7.34	0.0732
C (T _{calcination})	138.87	1	138.87	12.23	0.0396
D (Precursor)	699.50	1	699.50	61.61	0.0043
AC	634.68	1	634.68	55.90	0.0050
AD	211.49	1	211.49	18.63	0.0229
BC	121.64	1	121.64	10.71	0.0467
BD	208.68	1	208.68	18.38	0.0233
CD	169.38	1	169.38	14.92	0.0307
B ₂	601.15	1	601.15	52.95	0.0054
C ₂	144.60	1	144.60	12.74	0.0376
ABC	201.11	1	201.11	17.71	0.0245
ACD	1008.54	1	1008.54	88.83	0.0025
BCD	89.49	1	89.49	7.88	0.0674
A2B	86.46	1	86.46	7.62	0.0702
Residual	34.06	3	11.35		
Total	2260.58	18			

T_{precipitation} = 80°C (A=+1), T_{drying} = 115°C (B=0) and
T_{calcination} = 800°C (C=+1)

In summary, results of optimization showed that Ni-Nitrate is a more appropriate precursor than the Ni-Acetate to maximize the H₂ selectivity.

3.3.3 Analysis of variance of H₂ yield (X × S)

The ANOVA results of hydrogen yield are presented in Table 5. The relationship between the response and input factors was expressed by the following model, in which the factors were entered in coded values:

Table 5. ANOVA table of H₂ yield.

Source	Sum of Squares	df	Mean Square	F-Value	p-value Prob > F
Model	2.659E+007	1	3.323E+006	6.34	0.0044
A(T _{precipitation})	2.393E+006	1	2.393E+006	4.57	0.0584
D(Precursor)	1.819E+007	1	1.819E+007	34.69	0.0002
AC	1.220E+007	1	1.220E+007	23.27	0.0007
BC	3.331E+006	1	3.331E+006	6.35	0.0304
B ²	6.673E+006	1	6.673E+006	12.73	0.0051
C ²	5.258E+006	1	5.258E+006	10.03	0.0100
ACD	1.228E+007	1	1.228E+007	23.43	0.0007
BCD	2.494E+006	1	2.494E+006	4.76	0.0541
Residual	5.243E+006	10	5.243E+005		
Cor Total	3.183E+007	18			

$$H_2 \text{ yield (\%)} = +62.2132 + 4.5920A - 13.8136D + 15.9824AC + 5.8106BC - 16.2379B^2 - 14.3860C^2 + 17.5139ACD + 5.0173BCD$$

As mentioned above, A, B and C are the coded values of precipitation, drying and calcination temperatures, respectively, and D is the categorical term for the precursor type that is (-1) for Ni-Nitrate and (+1) for Ni-Acetate. The p-value is 0.0044, which indicates the model is significant. According to ANOVA results, the precursor is the most effective since precipitation temperature affects H_2 yield but drying and calcination temperatures have no significant effect. Results prove some interactional effects over H_2 yield by AC and BC.

To validate and test the obtained model, results obtained in the two previous sections were used for calculation of yield. At the base levels of the factors the model predicted the response 40.07 % and at zero levels 76.03 % while the response was 46.80 % and 72.53% in experimental tests, respectively. Therefore, it is concluded that the prediction is acceptable.

Figure 6 indicates the response of the model versus the effective parameters.

Figure 6a shows the results obtained by using Ni-Nitrate as the precursor. This figure demonstrates that the maximum H_2 Yield is obtained at a low level of precipitation temperature and moderate levels of calcination and drying temperatures. Therefore, to maximize the H_2 Yield, the optimum conditions are the following, approximately:

$$T_{\text{precipitation}} = 30^\circ\text{C} \text{ (A=-1)}, T_{\text{drying}} = 115^\circ\text{C} \text{ (B=0)}, T_{\text{calcination}} = 700^\circ\text{C} \text{ (C=0)}$$

Figure 6b shows the results obtained using Ni-Acetate as the precursor. This figure indicates that the maximum H_2 Yield is obtained at high levels of drying, precipitation and calcination temperatures. Therefore, optimum conditions are the following, approximately:

$$T_{\text{precipitation}} = 80^\circ\text{C} \text{ (A=+1)}, T_{\text{drying}} = 140^\circ\text{C} \text{ (B=+1)} \text{ and } T_{\text{calcination}} = 800^\circ\text{C} \text{ (C=+1)}$$

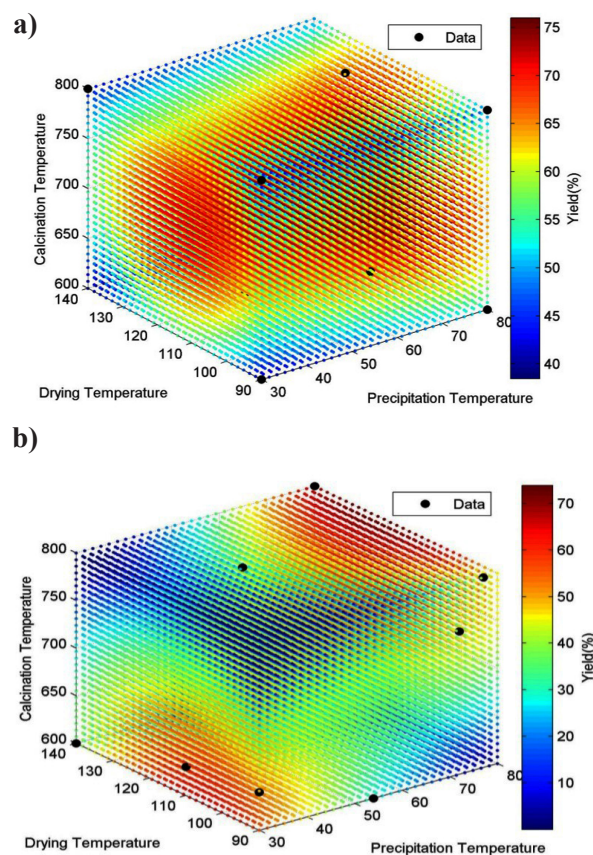


Fig. 6. The response surface of the data for H_2 yield with the catalyst using a) Ni-Nitrate as the precursor and b) Ni-Acetate as the precursor.

In summary, to maximize the H_2 Yield, results of optimization indicated that Ni-Nitrate is a more appropriate precursor than Ni-Acetate.

4. Conclusions

In this paper, the preparation process of Ni/Al_2O_3 catalyst was successfully optimized in order to maximizing conversion, Hydrogen selectivity and Hydrogen yield in steam reforming of n-butane. Results indicated that the nitrate precursor was more efficient than the acetate precursor. Although conversion and selectivity were optimized, Hydrogen yield was more favorable. Therefore, its optimum condition was selected as the global optimum condition for hydrogen

production via steam reforming of n-butane as follows:

$$T_{\text{precipitation}} = 30^{\circ}\text{C}, T_{\text{drying}} = 115^{\circ}\text{C}, T_{\text{calcination}} = 700^{\circ}\text{C}$$

5. Nomenclature

A	precipitation temperature of synthesized samples code;
AB	secondary interaction between A and B;
ABC	tertiary interaction between A, B and C;
ABD	tertiary interaction between A, B and D;
AC	secondary interaction between A and C;
ACD	tertiary interaction between A, C and D;
AD	secondary interaction between A and D;
B	drying temperature of synthesized samples code;
BC	secondary interaction between B and C;
BD	secondary interaction between B and D;
BCD	tertiary interaction between B, C and D;
C	calcination temperature of synthesized samples code;
CD	secondary interaction between C and D;
C_i	is concentration of i sample in input;
$C_{i\text{ out}}$	concentration of i sample in output;
D	precursor type;
H_2 yield	n- butane conversion $\times H_2$ selectivity;
l	actual value of factor;
l_0	null point of factor;
Δl	actual range of factor;
Ni	nickel
S	selectivity to H_2 ;
$T_{\text{precipitation}}$	precipitation temperature of synthesized samples;
T_{drying}	drying temperature of synthesized samples;
$T_{\text{calcination}}$	calcination temperature of synthesized samples
X	conversion

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