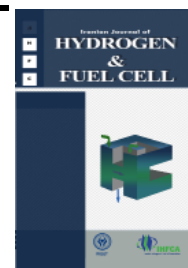


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A comparative study on the kinetics of carbon dioxide methanation over bimetallic and monometallic catalysts

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Abstract

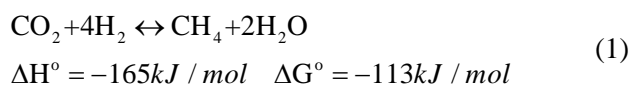
In this paper, Ni/Al and La-Ni/Al catalysts were prepared with a co-impregnation method and then employed in a carbon dioxide methanation reaction. The catalytic results showed that the catalyst with (10wt. %) lanthanum and (20wt.%) nickel had the highest activity at low temperatures in CO₂ methanation, and the La-Ni/Al catalysts changed the reaction path by lowering its activation energy and consequently increased the rate of reaction. Moreover, the kinetic behavior of the bimetallic and monometallic catalysts in the CO₂ methanation reaction was investigated as functions of partial pressures of H₂ and CO₂ in order to determine the changes in the parameters of power-law type rate expression resulting from the addition second metal to the catalyst and the change in the La/Ni ratio. The reaction orders (α and β) and the rate constant (k) were estimated by non-linear regression analysis that minimized the sum of the squared differences of calculated and experimental CO₂ methanation rates. The results showed that the reaction rate is more sensitive to H₂ partial pressure than CO₂ partial pressure.

1. Introduction

The increase of greenhouse gases (mainly CO₂) has caused to create the perilous problems in the atmosphere. Thus, great efforts have been recently made to implement suitable actions for capture and sequestration of CO₂. Technologies including utilization of CO₂ will be a key response strategy for protecting the environment [1].

There are different ways of adding value to CO₂. One

of them is hydrogenation to methane. The hydrogenation of carbon dioxide to methane over catalysts was described by Sabatier and Senderens more than 100 years ago as the following Eq. (1) [2-4].



The required hydrogen for this reaction is generated from renewable energy sources. Also, the methane produced by this reaction can be sent to a chemical

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industry or used as an energy carrier, which is a significant advantage for saving the methane. The methanation reaction has been studied over numerous supported metals catalysts, but especially Ni-based catalysts due to the low cost and abundance of nickel. In addition, different supports were used for dispersing nickel particles such as Al_2O_3 , TiO_2 , Pt, SiO_2 [3, 5-6] or zeolites [7]. Among them, the Ni/ Al_2O_3 catalyst shows the high catalytic activity and selectivity for methane in the methanation of carbon dioxide with hydrogen [8-9].

Recent studies have been focused on the methanation reaction at high temperatures ($>200^\circ\text{C}$). An important challenge in CO_2 reduction is the necessity of accomplishing the reaction at a low temperature, especially when CO_2 and/or H_2 sources are intermittent, in order to improve the flexibility of the operation and increase the energetic efficiency of the process [3]. Thus, the addition of a small amount of promoters such as Fe, Co, Ce, La [10-11], Mo and Cu can increase the stability and the activity of the nickel-based catalysts in a methanation reaction at low temperatures [10]. In fact, utilization of bimetallic catalysts arises from the beneficial effects of interaction between the two metals which causes an increase in both the activity and the selectivity of the catalysts [12]. The contributory interaction between the two metals has been explained by either the physical promotion provided by one of the metals or the electron transfer from one of the metal (or metal oxide) sites to the sites of the second metal [3, 12].

Despite the fact that the methanation reaction has been recognized for several decades, very few studies have focused on the kinetics of carbon dioxide methanation or the details of reaction mechanism.

In this work, the kinetic behavior of the bimetallic and monometallic catalysts in a CO_2 methanation reaction was investigated as functions of partial pressures of H_2 and CO_2 . Also, the kinetics of CO_2 methanation over these catalysts were investigated in order to determine the changes in the parameters of the power-law type rate expression, resulting from the addition of a second metal to the catalyst and the change in the La/Ni loading ratio. Conclusions from previous studies

are combined with the present kinetic results to derive a kinetic model for the methanation reaction [13].

2. Experimental

2.1. Starting materials

The starting materials were Ni $(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98% purity, Merck), La $(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99% purity, Merck) and aluminum tri isopropylate (98% purity, Merck) as Ni, La and Al precursors, respectively. All the materials were used as received without further purification.

2.2. Catalyst preparation

Ni/Al and La-Ni/Al catalysts were prepared according to the method explained in our previous work [13, 14]. In summary, $\gamma\text{-Al}_2\text{O}_3$ was prepared by the sol-gel method and used as support. For preparing the catalysts, certain amounts of Ni $(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and La $(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 25ml distilled water under stirring. Then, the dehydrated catalyst support was added to the prepared solution and stirred for 4h at room temperature. Nickel loading was fixed at 20wt. % and the La content was varied from 5 to 10wt. %. After that, the suspension was dried at 80°C for 10h and calcined at 450°C for 3h. In this process, the prepared bimetallic catalysts were denoted by M-Ni/Al, where M represents the second metal content in wt. %.

2.3. Catalytic activity tests

The catalytic performance tests of the methanation reaction were carried out in a tubular fixed bed reactor (10-mm I.D) made of quartz at atmospheric pressure. The reactor was placed in an electric furnace and the reaction temperature was measured by a thermocouple inserted in the middle of the catalyst bed. Prior to the reaction the catalyst was reduced under a flow of pure H_2 with (25ml/min) at 450°C for 2h. The flow rates of the entering gases were controlled by Brooks 5850E mass flow controllers. The gas composition at the

reactor outlet was analyzed with a gas chromatograph (Varian 3400) equipped with a TCD detector and a Carboxen 1000 column.

The schematic diagram of the catalytic test set-up is shown in Figure 1. The activity of the catalysts was calculated from the CO₂ conversion and the CH₄ selectivity according to Eq. (2) and (3) [10, 15-16]. Also, the kinetic measurements were performed under differential conditions at 350°C. The feed ratios of H₂/CO₂ were varied from 0.25 to 4 at a constant GHSV of 9000 ml/g_{cat}.h. Moreover, the Ar (inert gas) was used as a balance gas to keep the total flow constant.

$$X_{\text{CO}_2} (\%) = \left(1 - \frac{\text{CO}_2}{\text{CH}_4 + \text{CO} + \text{CO}_2} \right) \times 100 \quad (2)$$

$$S_{\text{CH}_4} (\%) = \left(\frac{\text{CH}_4}{\text{CH}_4 + \text{CO}} \right) \times 100 \quad (3)$$

3. Results and discussion

The methanation reaction was carried out over the monometallic and bimetallic catalysts to investigate the effect of the La addition on the catalytic performance.

The structural properties of the bimetallic catalysts were obtained by N₂ adsorption-desorption analysis and the results are presented in Table 1. As can be seen, the bimetallic catalysts possessed the possess a lower surface area than the monometallic catalyst. This can be related to the blocking of Al₂O₃ pores by the second metal. In addition, the results show a decrease

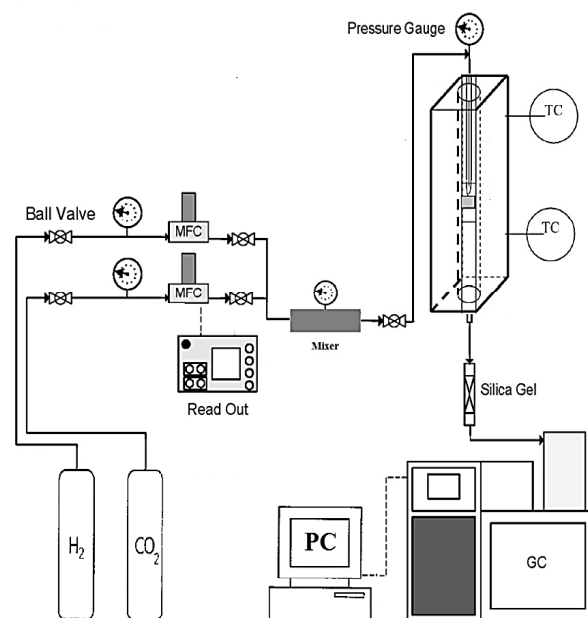


Fig. 1. Schematic diagram of the set-up for activity tests.

in the bimetallic catalysts pore size compared to that observed for the monometallic catalyst.

Figure 2 represents the CO₂ conversion and CH₄ selectivity as a function of reaction temperature. It shows that the addition of La to nickel catalyst had a dramatic effect on the CO₂ conversion. As can be seen, the CO₂ conversion of the La-Ni/Al catalysts at low temperatures is higher than those observed for the monometallic catalyst, due to the formation of dioxycarbonate La₂O₂CO₃ species caused by a reaction between lanthanum oxides and CO₂. The formation of dioxycarbonate La₂O₂CO₃ species led to increasing CO₂ conversion [11]. At lower temperatures, CO₂ conversion progressed well but increased the reaction temperature, then CO₂ conversion decreased due to the exothermic nature of the reaction. Therefore,

Table 1. Structural properties of xLa-20Ni/Al₂O₃ catalysts with the different lanthanum contents.

Catalyst	Lanthanum contents	Surface area ^a	Pore volume ^b	Pore diameter ^c
	(wt. %)	(m ² .g ⁻¹)	(cm ³ .g ⁻¹)	(nm)
20Ni/Al ₂ O ₃	0	143.3	0.36	7.4
	5	115.8	0.30	7.4
	10	107.9	0.29	7.5

^a Calculated by the BET equation.

^b BJH desorption pore volume.

^c BJH desorption average pore diameter.

CO₂ conversion increased as the reaction temperature increased from 200 to 300°C, but a further increase in reaction temperature decreased the CO₂ conversion.

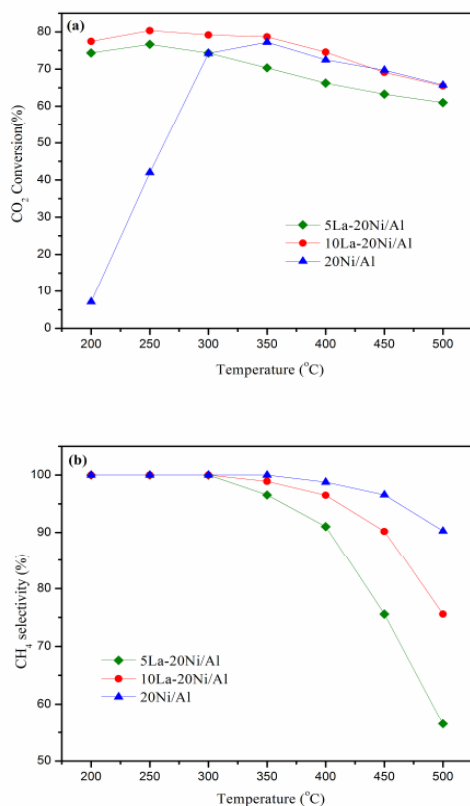


Fig. 2. Effect of the La addition on (a) CO₂ conversion and (b) CH₄ selectivity, GHSV= 9000 mL/g_{cat}·h, (H₂/CO₂) molar ratio= 3.5.

Moreover, CH₄ selectivity decreased as the reaction temperature increased, because other products (except CH₄) were obtained at high reaction temperatures. Also, Figure 2 shows the effect of lanthanum contents on the catalytic performance of 20Ni/Al catalyst. The catalytic results show that the CO₂ conversion and CH₄ selectivity increased when the lanthanum content increased from 5 to 10 wt.% at low temperatures.

Figure 3 shows the effect of different H₂/CO₂ molar ratios on the catalytic performance of the monometallic and bimetallic catalysts at 350°C. It is seen that the CO₂ conversion significantly increased as the H₂/CO₂ molar ratio increased. As can be seen, the 10La-20Ni/Al catalyst possessed the highest CO₂ conversion in

all feed ratios.

The kinetic behavior of the La-Ni/Al and Ni/Al catalysts in CO₂ methanation was investigated at 350°C as a function of partial pressures of CO₂ and H₂. The reaction rates in the kinetic measurements ($-r_{\text{CO}_2}$) were calculated from the conversion versus residence time ($w_{\text{cat}}/F_{\text{CO}_2}$) data according to Eq. (4) [17]:

$$-r_{\text{CO}_2} = \frac{x_{\text{CO}_2} F_{\text{CO}_2}}{W_{\text{cat}}} \quad (4)$$

Where, x_{CO_2} is the CO₂ conversion, F_{CO_2} is the CO₂ flow rate in the feed in ml/min converted to mmol/s, w_{cat} is the catalyst weight in g, and ($-r_{\text{CO}_2}$) is the reaction rate in mmol/g.s.

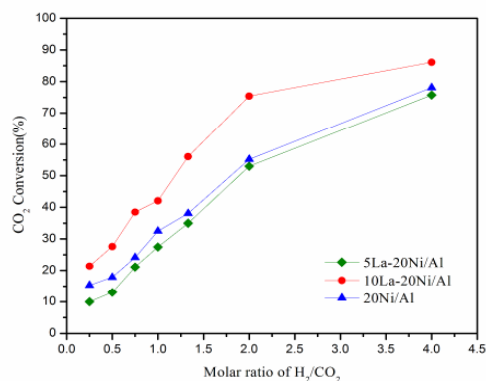


Fig. 3. Effect of (H₂/CO₂) molar ratio on catalytic performance at, 350°C, GHSV= 9000 mL/g_{cat}·h.

The activation energies were calculated over a temperature range of 200-300°C, based on the consumption rates of CO₂. The experimental data were taken after 60 min to ensure stable performance of the catalyst. The Arrhenius plots in Figure 4 give a comparison of activation energy values (E_a) over monometallic and bimetallic catalysts.

The activation energies were calculated from the slopes of these plots (Eq. (5)) where E_a is the activation energy and R is the rate of reaction. The obtained values are reported in Table 2.

$$\text{Slope} = -\frac{E_a}{R} \quad (5)$$

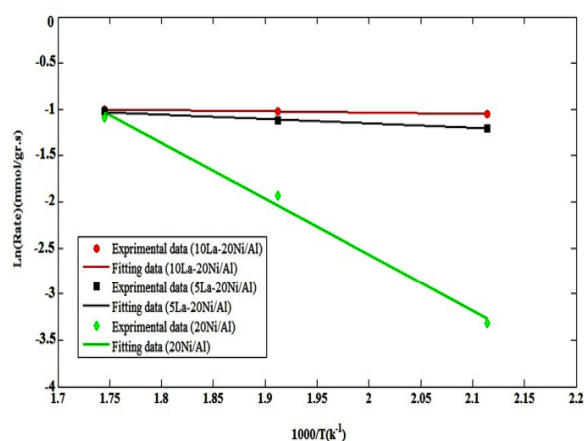


Fig. 4. Arrhenius plots for CO₂ consumption rates over monometallic and bimetallic catalysts.

It is remarkable that the activation energy for the monometallic catalyst is higher than those observed for the bimetallic catalysts. This means that the bimetallic catalysts change the reaction path by lowering the activation energy and increasing the rate of reaction. Also, the difference in the activation energies of 10La–20Ni/Al and 5La–20Ni/Al most probably stems from the different La/Ni ratios of these catalysts and the consequent change in the surface mechanism.

Table 2. Comparison of apparent activation energy (E_a , kJ/mol) over monometallic and bimetallic catalysts

E_a (CO ₂)(kJ/mol)	Catalyst
50.36	20Ni/Al
4.03	5La-20Ni/Al
1.2	10La-20Ni/Al

3.1. Effect of H₂ and CO₂ partial pressures on reaction rate

In chemical kinetics studies, after the rate data have been taken, a mechanism and a power-law rate model are proposed based on the data taken. Consequently, more than one mechanism and rate law may be in accordance with the data. In order to find the appropriate rate law, regression techniques are applied to identify which model equation best fits with the data by choosing one model with the minimum sum of squares.

Therefore, powerful regression techniques (methods) are used to determine the parameters for the proposed model. Regression techniques basically are linear regression, multiple regression, polynomial regression and non-linear regression. The common features of regression techniques are to make the minimum sum of the squares and to make the correction factor as close to unity as possible. Among the different types of regression techniques, the non-linear regression technique is in accordance with the equations for calculating the parameters of the proposed model. This method is very common and can be used almost under any conditions. General form is $y = f(x_1, x_2, \dots, x_n, a_1, a_2, \dots, a_n)$, where n = number of experiments, m = number of parameters to be determined providing $n > m + 1$. The rate parameters are calculated with this non-linear regression technique. Of course, the model parameters must be realistic. For example, the reaction rate constant must be positive and meaningful physically [17-18].

The kinetics of CO₂ methanation was investigated over bimetallic and monometallic catalysts where initial rates are taken at a constant temperature of 350°C and at various partial pressures of reactants under differential conditions in order to determine the effect of a second metal on kinetic behavior. In the experimental tests, the partial pressures of H₂ and CO₂ were varied from 0.02 to 0.08 and 0.08 to 0.02 atm, respectively by varying the flow rates of CO₂ and H₂, while the total pressure and flow rates were chosen 1 atm and 30 ml/min, respectively. The CO₂ conversion was calculated for seven different H₂/CO₂ ratios, and the reaction rates presented in Table 2 were calculated from Eq. (4) for both bimetallic and monometallic catalysts.

The power-law type rate expression applied for CO₂ methanation is given in Eq. (6):

$$-r_{\text{CO}_2} = k(P_{\text{H}_2})^\alpha (P_{\text{CO}_2})^\beta \quad (6)$$

The reaction orders (α and β) and the rate constant (k) were estimated by the non-linear regression technique by minimizing the sum of the squared differences of calculated and experimental CO₂ methanation rates

using the Levenberg–Marquardt algorithm.

The obtained results at various partial pressures at 350°C are used to estimate the reaction orders by the non-linear regression technique. The reaction orders and the minimum sum of the squared differences of calculated and experimental CO₂ methanation rates are given in Table 3. The results in Table 3 show that the reaction order of CO₂ for all catalysts is lower than the reaction order of H₂. The obtained orders for CO₂ and H₂ indicate that CO₂ was more strongly adsorbed

The effect of the CO₂ and H₂ partial pressure on the rate of carbon dioxide consumption also is presented in Figures 5 and 6.

As shown in these figures, fitting data was approximated by a linear function and there was a linear relationship between the CO₂ consumption rate and the CO₂ and H₂ partial pressure, and also the reaction rates increased as the partial pressures increased in the range of 0.02–0.08atm for all the catalysts. The points in these figures show the experimental results and

Table 3. Initial rates of CO₂ methanation at 350°C on Ni/Al and La-Ni/Al catalysts

Partial pressures (atm)		H ₂ /CO ₂	Reaction rate×10 ⁴ (mmol/g.s)		
H ₂	CO ₂		20Ni/Al	5La-20Ni/Al	10La-20Ni/Al
0.02	0.08	0.25	5.87	3.92	8.22
0.04	0.08	0.50	7.05	5.09	10.96
0.06	0.08	0.75	9.40	8.22	14.88
0.08	0.08	1.00	12.68	10.96	16.44
0.08	0.06	1.33	11.15	10.30	16.40
0.08	0.04	2.00	9.76	9.58	14.70
0.08	0.02	4.00	7.64	7.45	8.428

than H₂. Moreover, this indicates that the reaction rate is more sensitive to H₂ partial pressure than CO₂ partial pressure because the order for H₂ is higher than the order for CO₂.

As can be seen in Tables 3 and 4, higher rate values obtained over the 10La-20Ni/Al catalyst led to a higher k value compared to that obtained from other catalysts.

The results reveal that the performance of the 10La-20Ni/Al sample strongly depends on the H₂/CO₂ molar ratio. Due to its relatively higher content of La, which increases the metal particle dispersion on the support, the H₂ dependence is rather limited for the other catalysts.

the lines fitted the experimental data by the power-law type rate law Eq. (6). It can be observed that the experimental results and the proposed power type rate model for each catalyst are in good agreement.

3.2. Effect of CO addition on CO₂ methanation

In the methanation reaction, as the reaction temperature increased the CO₂ conversion, and CH₄ selectivity decreased, because CO₂ is converted to CO on the Ni surface (reverse water gas shift reaction) [13]. In order to realize the effect of the product on the chemical kinetic, carbon monoxide with different partial pressures was added to the feed stream while

Table 4. Estimated reaction rate parameters for monometallic and bimetallic catalysts

catalyst	Reaction orders		k×10 ²	σ ² (mmol/gr.s) ²
	α	β		
20Ni/Al	0.65	0.30	2.00(mmol/gr.s.atm ^{-0.95})	7.47×10 ⁻⁸
5La-20Ni/Al	0.59	0.23	1.30(mmol/gr.s.atm ^{-0.82})	6.42×10 ⁻⁸
10La-20Ni/Al	0.92	0.42	2.20(mmol/gr.s.atm ^{-1.34})	1.79×10 ⁻⁸

partial pressures of CO_2 and H_2 were kept constant at 0.08atm. The CO_2 consumption rate values in the presence of CO are given in Table 5 and Figure 7. As can be seen, there is an inhibiting and negative effect

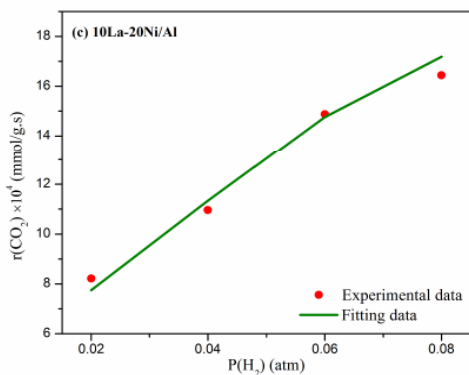
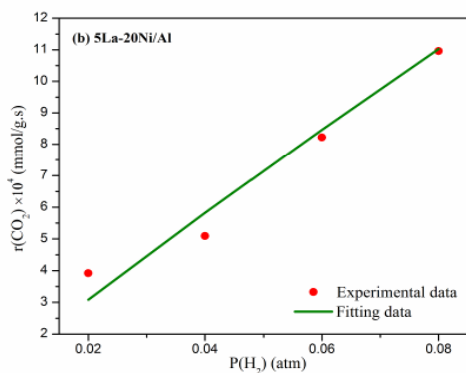
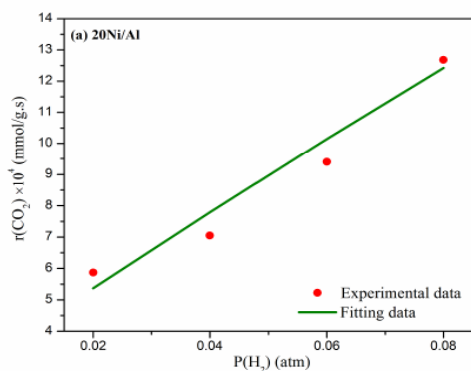


Fig. 5. CO_2 consumption rates as a function of the H_2 partial pressures on Ni/Al and La-Ni/Al catalysts.

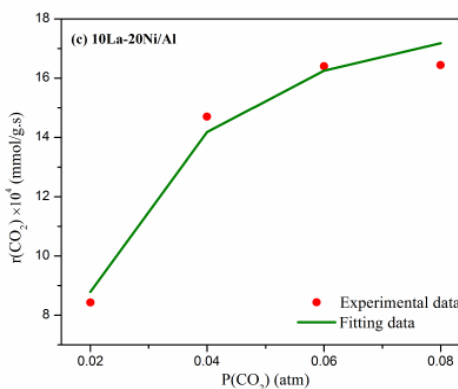
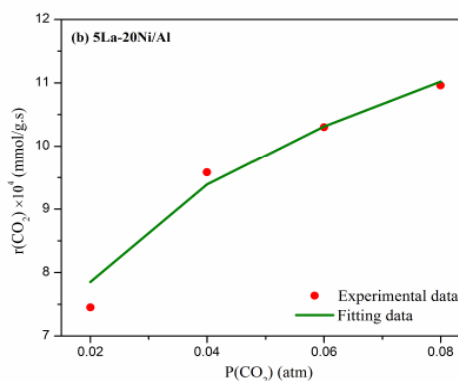
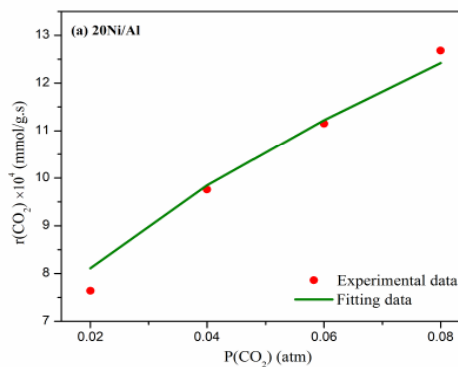


Fig. 6. CO_2 consumption rates as a function of the CO_2 partial pressures on Ni/Al and La-Ni/Al catalysts.

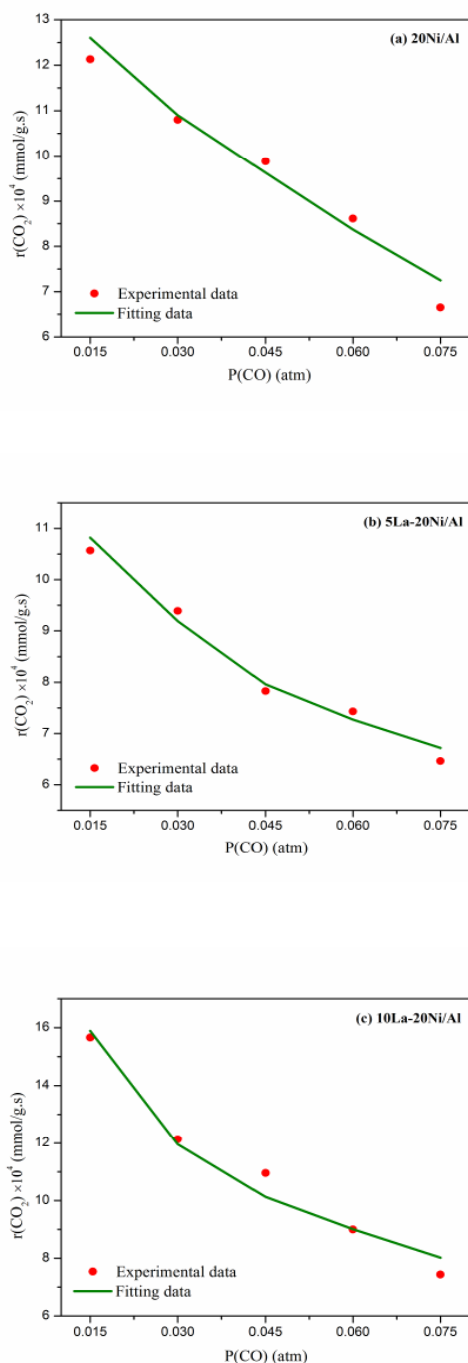


Fig. 7. CO₂ consumption rates as a function of the CO partial pressures on Ni/Al and La-Ni/Al catalysts.

on the carbon dioxide consumption rate. Therefore, an investigation of CO effect on the reaction rate is necessary. The power-law type rate expression applied for CO₂ methanation in the presence of CO is given in

Eq. (7):

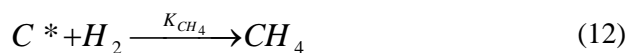
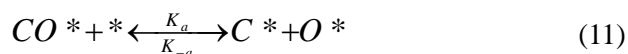
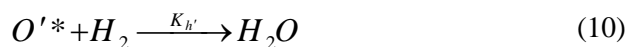
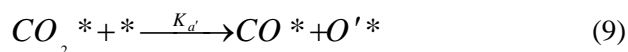
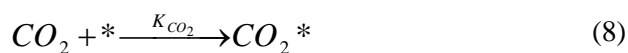
$$-r_{\text{CO}_2} = k(P_{\text{H}_2})^\alpha (P_{\text{CO}_2})^\beta (P_{\text{CO}})^\delta \quad (7)$$

The reaction rate parameters (k and δ) were determined by using the nonlinear regression technique and the Levenberg–Marquardt algorithm, their values are reported in Table 6. It should be mentioned that the reaction orders for CO₂ and H₂ were assumed the same as with “CO₂ methanation without CO”. As can be seen, the addition of carbon monoxide changes the k value.

The negative and inhibiting effect of CO on reaction rate can be attributed to the blocking of some of the CO₂ adsorption sites on the support, and the strong interaction of CO with the catalytic surface compared to CO₂ [14].

3.3. Proposed mechanism

The kinetics of CO₂ methanation is expressed by a power-law model in previous sections. Due to its simplicity in application and the wide range of partial-pressure data, this model may be inadequate. Thus, it becomes necessary to investigate other models which can express the kinetics of the methanation reaction. Hakuai Inoue and Masaki Funakoshi proposed a model for the methanation of carbon dioxide in 1984 [19]. In this model, the rate of reaction is expressed by a Langmuir adsorption isotherm and the reaction steps are written as follows:



Adsorption of reactants on the surface of the catalyst is the first step in every reaction of heterogeneous

Table 5. Effect of CO partial pressure on CO₂ methanation rates

Partial pressures (atm)			Reaction rate×10 ⁴ (mmol/g.s)		
H ₂	CO ₂	CO	20Ni/Al	5La-20Ni/Al	10La-20Ni/Al
0.08	0.08	0.015	12.13	10.57	15.66
0.08	0.08	0.030	10.8	9.39	12.14
0.08	0.08	0.045	9.88	7.83	10.96
0.08	0.08	0.060	8.613	7.63	9.00
0.08	0.08	0.075	6.65	6.464	7.44

Table 6. Estimated reaction rate parameters in the presence of CO

Catalyst	Reaction order of CO	k×10 ²	Power-type rate law
20Ni/Al	-0.29	0.48	-r _{CO₂} = k(P _{H₂}) ^{0.65} (P _{CO₂}) ^{0.3} (P _{CO}) ^{-0.29}
5La-20Ni/Al	-0.28	0.31	-r _{CO₂} = k(P _{H₂}) ^{0.59} (P _{CO₂}) ^{0.23} (P _{CO}) ^{-0.28}
10La-20Ni/Al	-0.41	1.2	-r _{CO₂} = k(P _{H₂}) ^{0.92} (P _{CO₂}) ^{0.42} (P _{CO}) ^{-0.41}

catalysis. In Eqs. (8) and (9), carbon dioxide is adsorbed on the surface of the catalyst but hydrogen adsorption has no main part kinetically in this reaction. At steady state:

$$\frac{d\theta_{CO_2}}{dt} = k_{CO_2} P_{CO_2} \theta_v - k_{-CO_2} \theta_{CO_2} \quad (14)$$

$$\rightarrow \theta_{CO_2} = K_{CO_2} P_{CO_2} \theta_v$$

$$k_a \theta_{CO_2} \theta_v - k_{-a} \theta_{CO} \theta_{O'} = 0 \quad (15)$$

$$\rightarrow \theta_{CO} \theta_{O'} = K_a \theta_{CO_2} \theta_v$$

The rate of disappearance of carbon dioxide is equal to the rate of the reaction (10) to produce water at the steady state.

$$-r_{CO_2} = K_h \theta_{O'} P_{H_2} \quad (16)$$

$$(K_h K_a K_{CO_2}) P_{H_2} P_{CO_2} \theta_v^2 / \theta_{CO}$$

During the reaction, CO is produced as an intermediate. Therefore, it is necessary to consider the interaction of both reactions.

$$\frac{d\theta_C}{dt} = K_a \theta_{CO} \theta_v - K_{-a} \theta_C \theta_{O'} - K_{CH_4} P_{H_2} \theta_C$$

At steady state conditions:

$$K_a \theta_{CO} \theta_v - K_{-a} \theta_C \theta_{O'} - K_{CH_4} P_{H_2} \theta_C = 0 \quad (17)$$

The rate of methane and water production should be equal:

$$r_{CH_4} = K_{CH_4} P_{H_2} \theta_C \quad (18)$$

$$r_{12} = r_{13} \rightarrow$$

$$K_{CH_4} P_{H_2} \theta_C = K_h P_{H_2} \theta_{O'}$$

$$\theta_{O'} = \alpha \theta_C \quad \alpha = K_{CH_4} / K_h \quad (19)$$

Therefore, from Eqs. (17) and (19), θ_C is obtained as follows:

$$\theta_C^2 + (K_{CH_4} P_{H_2} / \alpha K_{-a}) \theta_C - (K_a / \alpha K_{-a}) \theta_{CO} \theta_v = 0$$

$$\theta_C = \sqrt{(K_{CH_4} P_{H_2} / 2\alpha k_{-a})^2 + (K_a / \alpha K_{-a}) \theta_{CO} \theta_v} - (K_{CH_4} P_{H_2} / 2\alpha K_{-a}) \quad (20)$$

Because the adsorption of CO is strong, it can be assumed:

$$(K_a / \alpha K_{-a}) \theta_{CO} \theta_v \geq (K_{CH_4} P_{H_2} / 2\alpha k_{-a})$$

Therefore, the rate of methanation is obtained from Eqs. (18) and (20):

$$r_{CH_4} = K_{CH_4} P_{H_2} \theta_C$$

$$r_{CH_4} = K_{CH_4} P_{H_2} [(K_a' / \alpha) \theta_{CO} \theta_v]^{1/2}$$

$$K_a' = K_a / K_{-a} \quad (21)$$

The carbon dioxide consumption rate is equal to the methanation rate.

$$r_{CH_4} = -r_{CO_2} \rightarrow K_{CH_4} P_{H_2} [(K_a' / \alpha) \theta_{CO} \theta_v]^{1/2} = (K_h' K_a' K_{CO_2}) P_{H_2} P_{CO_2} \theta_v^2 / \theta_{CO}$$

$$\theta_{CO} = \left[K_h' K_a' K_{CO_2} / (K_{CH_4} (K_a' / \alpha)^{1/2}) \right]^{2/3} \theta_v P_{CO_2}^{2/3} \quad (22)$$

$$-r_{CO_2} =$$

$$(K_{CH_4}^2 K_h' K_a' K_{CO_2} / \alpha)^{1/3} P_{H_2} \theta_v P_{CO_2}^{1/3}$$

On the other hand, the assumption is given that

$$\theta_{CO_2}, \theta_{H_2} \geq \theta_{H_2O}, \theta_C, \theta_O$$

$$\theta_v = \frac{1}{(1 + K_{CO_2} P_{CO_2} + K_{H_2} P_{H_2})}$$

Therefore, the consumption carbon dioxide rate becomes as follows:

$$-r_{CO_2} = \frac{(K_{CH_4}^2 K_h' K_a' K_{CO_2} / \alpha)^{1/3} P_{H_2} P_{CO_2}^{1/3}}{1 + K_{CO_2} P_{CO_2} + K_{H_2} P_{H_2}} \xrightarrow{\alpha = K_{CH_4} / K_h} -r_{CO_2} = \frac{(K_{CH_4} K_h' K_h K_a' K_{CO_2})^{1/3} P_{H_2} P_{CO_2}^{1/3}}{1 + K_{CO_2} P_{CO_2} + K_{H_2} P_{H_2}} \quad (23)$$

In order to analyze whether there is a change in reaction kinetics depending on the addition of a second metal, experimental CO₂ consumption rate data for all of the catalysts were fitted to the kinetic model represented in Eq. (23). The kinetic parameters are obtained by using the nonlinear regression technique and Levenberg-Marquardt algorithm.

The adsorption constants of methanation reaction for all catalysts are given in Table 7. The results show that the 10LA-20Ni/Al catalyst has a smaller error compared to the other catalysts. Hence, for this catalyst, the model proposed in Eq. (23) best fitted with the experimental data.

4. Conclusion

A series of monometallic catalyst (Ni/Al) and bimetallic catalysts (La-Ni/Al) with different lanthanum contents were prepared by the co-impregnation method and employed in CO₂ methanation. The experimental results showed that the activity of the Ni/Al catalyst in CO₂ methanation was significantly affected by the addition of the second metal to the catalyst at low

Table 7. The obtained adsorption constants for the methanation rate Eq. (23)

Catalysts	Rate parameter	$\sigma^2(\text{mmol/gr.s})^2$
20Ni/Al	$K_{\text{CH}_4} = 8.18 \text{mmol.gr}^{-1}.\text{s}^{-1}.\text{atm}^{-1}$	5.6×10^{-8}
	$K_{h'} = 0.27 \text{mmol.gr}^{-1}.\text{s}^{-1}.\text{atm}^{-1}$	
	$K_h = 0.14 \text{mmol.gr}^{-1}.\text{s}^{-1}.\text{atm}^{-1}$	
	$K_a = 0.41 \text{mmol.gr}^{-1}.\text{s}^{-1}$	
	$K_a' = 0.013$	
	$K_{\text{CO}_2} = 0.028 \text{atm}^{-1}$	
5La-20Ni/Al	$K_{\text{H}_2} = 0.69 \text{atm}^{-1}$	2.82×10^{-9}
	$K_{\text{CH}_4} = 7.91 \text{mmol.gr}^{-1}.\text{s}^{-1}.\text{atm}^{-1}$	
	$K_{h'} = 0.26 \text{mmol.gr}^{-1}.\text{s}^{-1}.\text{atm}^{-1}$	
	$K_h = 0.197 \text{mmol.gr}^{-1}.\text{s}^{-1}.\text{atm}^{-1}$	
	$K_a = 0.39 \text{mmol.gr}^{-1}.\text{s}^{-1}$	
	$K_a' = 0.013$	
10La-20Ni/Al	$K_{\text{CO}_2} = 0.03 \text{atm}^{-1}$	1.67×10^{-9}
	$K_{\text{H}_2} = 2.46 \text{atm}^{-1}$	
	$K_{\text{CH}_4} = 10.67 \text{mmol.gr}^{-1}.\text{s}^{-1}.\text{atm}^{-1}$	
	$K_{h'} = 0.27 \text{mmol.gr}^{-1}.\text{s}^{-1}.\text{atm}^{-1}$	
	$K_h = 0.20 \text{mmol.gr}^{-1}.\text{s}^{-1}.\text{atm}^{-1}$	
	$K_a = 0.40 \text{mmol.gr}^{-1}.\text{s}^{-1}$	
10La-20Ni/Al	$K_a' = 0.013$	1.67×10^{-9}
	$K_{\text{CO}_2} = 0.027 \text{atm}^{-1}$	
	$K_{\text{H}_2} = 2.67 \text{atm}^{-1}$	

temperatures. Also, the bimetallic catalysts changed the reaction path by lowering its activation energy and consequently increased the rate of reaction. In addition, the kinetic of CO₂ methanation was investigated over bimetallic and monometallic catalysts as a function of H₂ and CO₂ partial pressures with the analysis of the reaction rate data. The parameters of CO₂ consumption rate expressed by the power-law rate model and its results showed that the reaction rate was more sensitive to H₂ partial pressure than CO₂ partial pressure because the order of reaction for H₂ is higher than CO₂. On the other hand, with the addition of La and an increase in La/Ni ratio, the CO₂ adsorption became stronger and the addition of CO to the feed stream indicated that CO as a product had an inhabiting and negative effect on the reaction rate.

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Nomenclature

K_{CO_2}	Adsorption equilibrium constant of carbon dioxide
K_a	Equilibrium constant of Eq. (9)
K_h	Rate constant of Eq. (10)
*	Active site
K_a	Rate constant of forward reaction in Eq. (11)
K_{-a}	Rate constant of reverse reaction in Eq. (11)
K_{CH_4}	Rate constant of Eq. (12)
K_h	Rate constant of Eq. (13)
θ_{CO_2}	Fractions of active sites occupied by adsorbed carbon dioxide
θ_v	Fraction of vacant active sites
θ_C	Fractions of active sites occupied by adsorbed carbon
θ_{CO}	Fractions of active sites occupied by adsorbed carbon monoxide
θ_O	Fractions of active sites occupied by adsorbed oxygen

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