

CARBON DIOXIDE REFORMING OF METHANE ON SUPPORTED NICKEL CATALYSTS

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The reforming of CH₄ with CO₂ using various Ni catalysts has been investigated. As a result of screening tests, the selection of supports was found to be very important to control the catalytic activity of Ni. Among the various supports, ceramic foam and Al₂O₃ supports incorporating industrial steam reforming catalysts showed higher activities than SiO₂ supports. The kinetic study has shown that the results could be expressed by a simple power-law equation for the three activated catalysts. The effect of the support was also studied. The results showed the importance of the acid-base property of the catalyst.

Introduction

At the present time, great attention is being paid to global environmental problems such as the green house effect. The reduction of green house gasses such as CO₂ and CH₄ is therefore becoming more and more necessary. The reforming of CH₄ with CO₂ (Eq.(1)) is a particularly efficient process for producing synthesis gas from two green house gasses.



A reverse water-gas shift reaction occurs as a side reaction.



Synthesis gas is generally produced by steam reforming which is the reaction between H₂O and CH₄.



The synthesis gas, produced by the reaction between CO₂ and CH₄, has a high CO content which is effective for the synthesis of valuable oxygenated chemicals.

Natural gas which is produced mainly in South-East-Asia contains a large amount of CO₂⁷⁾. It remains unused due to this high CO₂ content. Methane can also be produced through the anaerobic methane fermentation of industrial waste water, and CO₂ is a co-product during this process. In these cases, CO₂ reforming of CH₄ is considered to be the most effective method.

Previous investigations of the reaction between CH₄ and CO₂ have mainly dealt with the screening test of catalysts. Sodesawa *et al.*¹⁷⁾ compared the catalytic activities of Ni-SiO₂, CuO and Fe₂O₃. Ni-SiO₂ indicated the highest activity and selectivity among them while other catalysts deactivated rapidly due to carbon deposition. Tokunaga *et al.*²¹⁾ also compared the activities of some

transition metal catalysts(Ni, Fe and Co) supported on Al₂O₃. Ni-Al₂O₃ was found to be an active catalyst. Gadalla *et al.*³⁻⁵⁾ tested the effect of supports and found that the industrial Ni catalyst supported on CaO-TiO₂-Al₂O₃ showed activity for a period over 40 hours. They also reported the solid state reaction of the support which decreased the surface area of the catalyst during the reaction. Supported noble metal catalysts were also investigated, especially over Rh^{2, 16, 19)}. Sakai *et al.*¹⁶⁾ tested the reaction of CO₂ with various hydrocarbons over supported Rh catalyst. Methane was found to give the highest reaction rate among the tested hydrocarbons. Rostrup-Nielsen and Hansen compared the catalytic activities for steam and CO₂ reforming of CH₄ by using Ni, Ru, Rh, Pd, Ir and Pt catalysts¹⁴⁾. They have pointed out that there would be no significant effect on the reforming mechanism when H₂O was replaced by CO₂. These studies suggested the importance of the selection of the supports as well as the active components.

Some of the screening tests presented simple power law equations. The reaction kinetics have been reported over Ni^{16, 21)}, Rh^{2, 12)} and Pt¹⁹⁾. But neither the kinetics nor the reaction mechanism of supported Ni catalyst have yet been reported in detail.

In this study, several kinds of Ni catalysts supported on Al₂O₃ or SiO₂ were compared. The kinetics of CO₂ reforming were also investigated for activated catalysts. The role of the support was then discussed.

1. Experimental

1.1 Experimental apparatus

The reaction was conducted in a conventional continuous flow reactor at atmospheric pressure as shown in Fig. 1. A thermocouple well was placed in the center of

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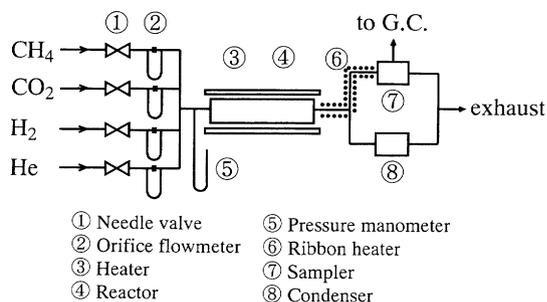


Fig. 1 Experimental apparatus

Table 1. Catalysts tested

Catalyst	Ni content [wt%]	Support/co-catalyst	Surface area [m ² /kg]	Remarks
A	55	SiO ₂ ,MgO	1.23×10 ⁵	a)
B	63	Al ₂ O ₃ ,CeO ₂ ,Ca ₂ O ₃ ,La ₂ O ₃	1.50	a)
C	44	SiO ₂	1.46	b)
D	60	SiO ₂	1.26	b)
E	40	Al ₂ O ₃	1.19	c)
F	26.7	Al ₂ O ₃ coated cordierite	0.20	a)
G	40	SiO ₂	3.66	c)

a) Industrial steam reforming catalyst was provided.

b) Industrial methanation catalyst was provided.

c) Reference catalyst was used as support and Ni was impregnated.

the quartz glass reactor. A pressure manometer was positioned at the entrance of the reactor and could be used as an emergency pressure relief valve. The gas sampler at the exit was maintained at 350 K to prevent condensation of water. All of the products were analyzed with a TCD gas chromatograph with a series of columns of 1.2 m of Porapak Q, 3 m of activated carbon and 1 m of silica gel, and were operated at 408K.

1.2 Catalysts

Table 1 shows the catalysts tested in this study. All of them are Ni catalysts supported on Al₂O₃ or SiO₂. As can be seen from **Table 1**, each catalyst was loaded with over 26.7wt% of excess Ni. Catalysts A and B are industrial catalysts for steam reforming while catalysts C and D are typical industrial methanation catalysts. Catalysts E and G were prepared by a conventional impregnation method from aqueous solution of nickel nitrate and Al₂O₃ (JRC-ALO-4 which was supplied by the Catalysis Society of Japan as a reference catalyst) and SiO₂ (JRC-SIO-5) were used as supports. Catalyst F was prepared by doping Ni on a three-dimensional framework of spongy cordierite coated with Al₂O₃. The cordierite consisted of Al₂O₃ (54wt%), SiO₂ (37wt%), MgO (6wt%) and others (3wt%). The porous mediums can convert energy between flowing gas enthalpy and thermal radiation effectively. They were recognized as energy converters in a new energy saving system which uses thermal radiation. Such energy conversion systems are applied as high-performance radiant reactors. Thus, this support can be used in a new type of radiant heating catalytic reaction. The porous mediums have other advantages such as thermal and chemical

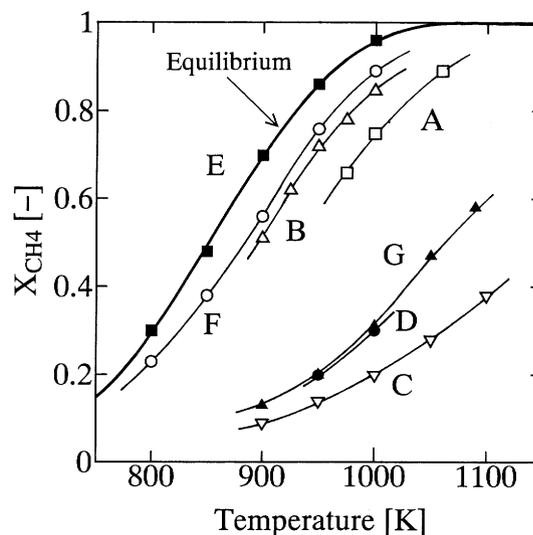


Fig. 2 Comparison between catalytic activities
Keys used in this figure (A-G) are the same as those in **Table 1**

CO₂/CH₄ = 2.0, W/F_{CH₄0} = 15.0s·kg-cat/mol, p_{CH₄} = 3.38 × 10⁴Pa, p_{CO₂} = 6.76 × 10⁴Pa

resistance and lower pressure drops.

BET surface areas were measured using nitrogen as an adsorption gas. Each catalyst was crushed and sieved to 20-32 mesh and diluted with quartz sands of the same size. Pre-reduction of catalysts was carried out under a flow of hydrogen at a rate of 5.0 × 10⁻⁷ m³/s at 1073 K for one hour.

2. Results

2.1 Comparison of catalytic activity

The catalytic activities were tested at temperatures ranging from 800 to 1200 K with a constant molar ratio of CO₂/CH₄ = 2.0. The results are shown in **Fig. 2**. The thick solid line in **Fig.2** shows the thermodynamic equilibrium conversion of CH₄. The calculation of the equilibrium compositions for complex reactions was carried out with reference to the literature⁶⁾. In spite of the high loading of Ni on the catalysts, the activity for CO₂ reforming of CH₄ was considerably affected by the kind of support. Alumina supported catalysts(B,E,F) show higher activities than SiO₂ supported catalysts(C,D,G). Catalyst E has the highest activity which overlaps the equilibrium curve. The activity of catalyst A, (nickel supported on SiO₂ with MgO) is similar to that of Al₂O₃-supported catalysts. This indicates that addition of MgO to SiO₂ increases the catalytic activity. The reason will be described in the section of discussions. The results indicate that industrial steam reforming catalysts(A,B,F) were more favorable for this reaction than methanation catalysts(C,D) and that Al₂O₃ was an efficient support.

2.2 Durability of the catalyst

The durability of the catalyst was tested by the following procedures which were represented as a cycle in this paper.

1) At first, the temperature of the catalyst bed was

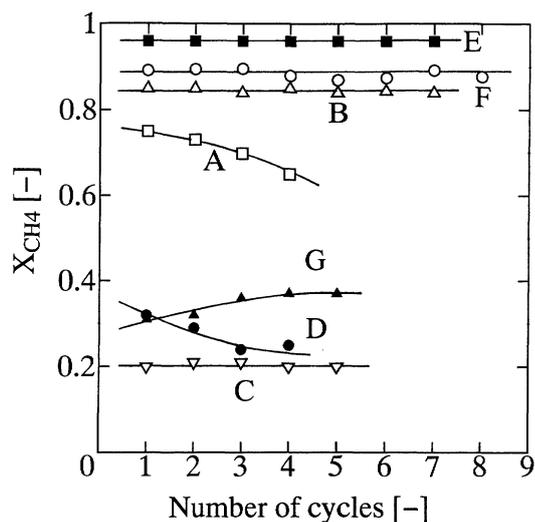


Fig. 3 Durability of the catalyst
 1000K, $\text{CO}_2/\text{CH}_4 = 2.0$, $W/F_{\text{CH}_4,0} = 15.0\text{s}\cdot\text{kg}\cdot\text{cat}/\text{mol}$,
 $p_{\text{CH}_4} = 3.38 \times 10^4\text{Pa}$, $p_{\text{CO}_2} = 6.76 \times 10^4\text{Pa}$

increased from room temperature to 1000 K under helium flow. The reaction was then started by feeding the reaction gas mixtures.

2) The reaction was carried out under various conditions for 10 hours. At the beginning and end of this reaction period, the activity of the catalyst was measured under the standard reaction condition for the reference run: 1000 K, $\text{CO}_2/\text{CH}_4 = 2.0$, $W/F_{\text{CH}_4,0} = 15.0(\text{s}\cdot\text{kg}\cdot\text{cat})/\text{mol}$.

3) The reaction gas mixtures were switched to helium flow in order to stop the reaction. The temperature of the catalyst bed was then lowered to room temperature.

Figure 3 shows the changes in catalytic activity with the number of repeated cycles mentioned above. The catalytic activity in this figure is represented by the reference run carried out under the standard condition which was conducted at the beginning of each cycle. Deactivation took place on catalysts A and D while the other catalysts showed stable activities. In the case of catalyst A, plugging of the reactor occurred because of a serious accumulation of carbonaceous deposit. Air oxidation of the deactivated catalysts(A, D) was carried out at 873 K for five hours to remove the carbonaceous deposit. This procedure regenerated the activity of catalyst A. However, the activity of catalyst D was not regenerated by oxidation. The deactivation of catalyst D was therefore attributed to the irreversible transformation of the catalyst.

These results, as shown in Figs. 2 and 3, indicate that the desirable catalysts for this reaction were catalysts B, E and F which were all supported on Al_2O_3 . In the following sections, the nature of catalysts E and F was tested. Catalyst A was used as a comparison.

2.3 Effect of $W/F_{\text{CH}_4,0}$

Figure 4 shows the effect of the time factor $W/F_{\text{CH}_4,0}$ over catalyst E. The conversion of CH_4 and the yield of H_2 and CO increased with $W/F_{\text{CH}_4,0}$ and reached equilibrium at $W/F_{\text{CH}_4,0} = 1.5(\text{s}\cdot\text{kg}\cdot\text{cat})/\text{mol}$. Based on stoichiometry, an equimolar amount of H_2 and CO should be produced

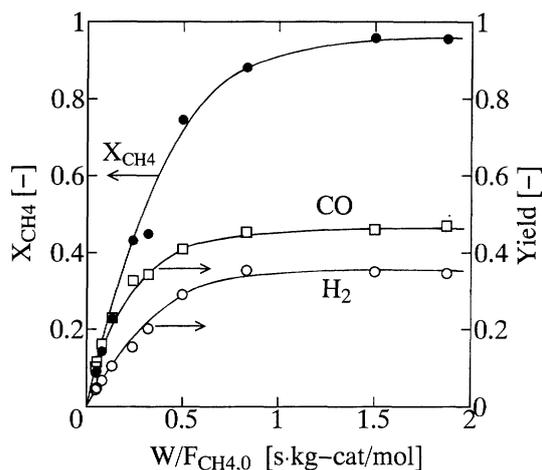


Fig. 4 Effect of $W/F_{\text{CH}_4,0}$
 Catalyst E, 1000K, $\text{CO}_2/\text{CH}_4 = 2.0$, $p_{\text{CH}_4} = 3.38 \times 10^4\text{Pa}$, $p_{\text{CO}_2} = 6.76 \times 10^4\text{Pa}$

according to(1) but the observed ratio of H_2/CO reached about 0.7. This was due to the occurrence of the reverse water-gas shift reaction (2).

2.4 Effect of the feed ratio of CO_2/CH_4

The ratio of reactants CO_2/CH_4 was changed from 0.5 to 5.0. The results for catalyst E are shown in **Fig. 5**. Thick solid lines in the figure show the conversion of CH_4 and the yields of each product at equilibrium. The experimental values agreed well with the calculations meaning no side reaction except(2) took place under the reaction conditions employed. Conversion of CH_4 increases with the increase of feed ratio of CO_2/CH_4 . An equimolar amount of H_2 and CO was produced at a CO_2/CH_4 ratio of 0.5. When the feed ratio was larger than 1.0, the yield of H_2 became lower because H_2 reacted with excess CO_2 through the reverse water-gas shift reaction. A lower CO_2/CH_4 ratio was preferred in order to increase the selectivity to H_2 while carbonaceous deposition might occur on the catalyst under such conditions.

2.5 Effect of the partial pressure of reactants

Kinetic studies were carried out with catalysts A, E and F to determine the rate equation. The reaction rate was measured with a differential reactor. The dependence of the reaction rates on the partial pressure of two reactants was investigated.

The effect of partial pressure of CH_4 on the reaction rate is shown in **Fig. 6**. The partial pressure with respect to CH_4 was changed from 16.9 to 50.7 kPa by adjusting the partial pressure of He. The reaction rates of catalyst A and E are only slightly superior to the that of catalyst F. The apparent reaction orders with respect to CH_4 partial pressure were found to be 1.0 for catalysts E and F and 0.8 for catalyst A.

The effect of partial pressure with respect to CO_2 is shown in **Fig. 7**. Carbon dioxide partial pressure was changed from 8.4 to 67.6 kPa. The partial pressure of CO_2 has no influence on the reaction rate. However, when the CO_2 partial pressure was lower than 8.4 kPa, the reaction order

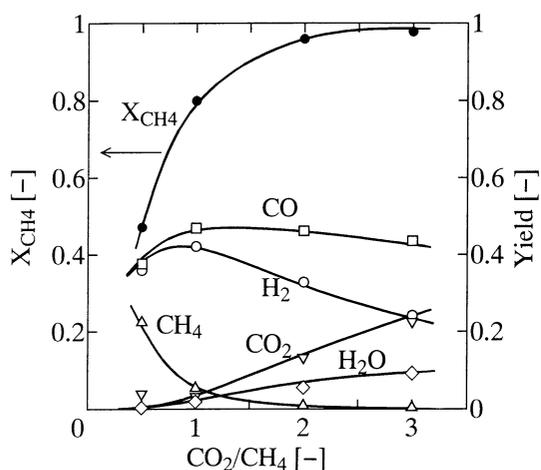


Fig. 5 Effect of the feed ratio on the conversion of CH_4 and the product distribution
The lines in the figure show the calculated conversion and the yields of each product
Catalyst E, 1000K, $W/F_{\text{CH}_4,0} = 1.88\text{s}\cdot\text{kg}\cdot\text{cat}/\text{mol}$

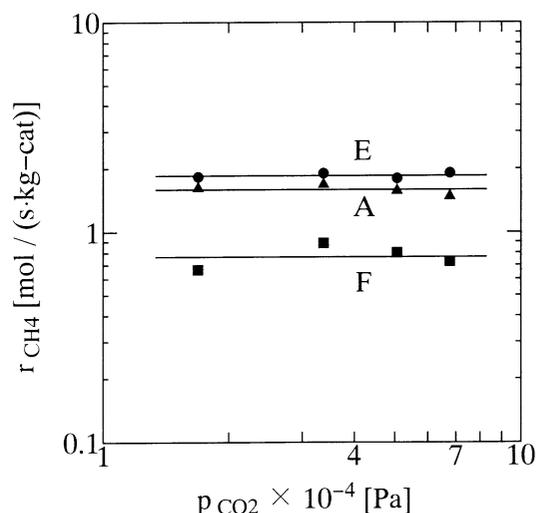


Fig. 7 Effect of partial pressure of CO_2 on the reaction rate
1000K, $p_{\text{CH}_4} = 3.38 \times 10^4\text{Pa}$

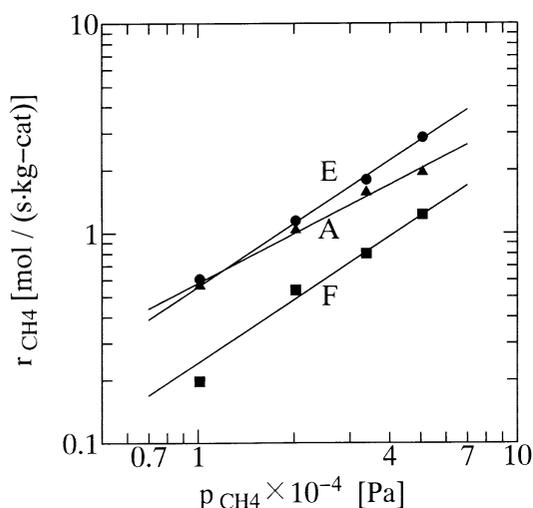


Fig. 6 Effect of partial pressure of CH_4 on the reaction rate
1000K, $p_{\text{CO}_2} = 5.07 \times 10^4\text{Pa}$

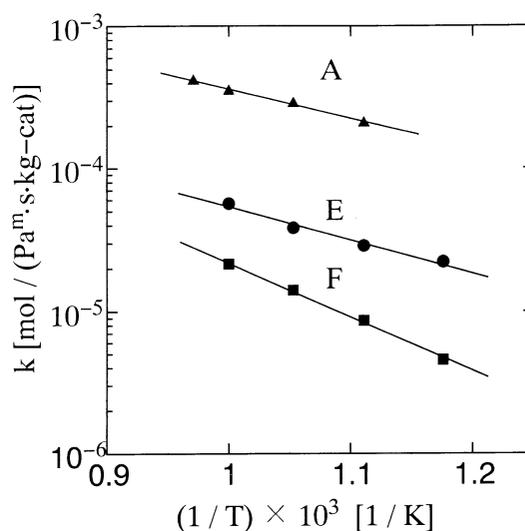


Fig. 8 Arrhenius plots

with respect to CO_2 for the catalyst E was almost 1.0.

The reaction rate can be expressed approximately through the following simple power-law equation in terms of the partial pressure of CH_4 .

$$-r_{\text{CH}_4} = k p_{\text{CH}_4}^m \quad (m = 0.8 - 1.0) \quad (4)$$

2.6 Effect of reaction temperature

Arrhenius plots are shown in **Fig. 8**. The reaction temperature was changed from 850 to 1030 K. The order of activation energy is as follows; SiO_2 with MgO (catalyst A), Al_2O_3 (catalyst E) < Al_2O_3 coated over cordierite (catalyst F).

3. Discussions

Table 2 compares the kinetic parameters of CO_2

reforming of CH_4 over supported Ni catalysts in this study and in other publications^{14, 16, 21}). Under practical reaction conditions, the apparent reaction orders were almost the same as those reported by Rostrup-Nielsen and Hansen¹⁴). They also reported that the reaction order with respect to CO_2 approached 1.0 at low CO_2/CH_4 ratios. Some of the results which showed different reaction orders were obtained under low partial pressures of CH_4 and CO_2 due to the use of an excess of inert gas^{16, 21}). These dependencies on the CO_2 partial pressure suggested strong adsorption of CO_2 on to the catalyst surface.

Rostrup-Nielsen and Hansen¹⁴) have also suggested that there would be no significant difference in the reaction mechanism between steam and CO_2 reforming reactions : (1) the dissociated oxygen from steam would oxidize methane when it was transferred to the activated CH_4 on the catalyst metal : and (2) the dissociated oxygen

Table 2. Comparison of kinetic parameters over Ni catalysts

Reference	Catalyst	$m^*)$	$n^*)$	$E^{**})$ [kJ/mol]	$k_0^{**})$ [mol/(Pa ^m ·s·kg-cat)]
This work	Ni-SiO ₂ (A)	0.8	0	40.1	4.50×10 ⁻²
	Ni-Al ₂ O ₃ (E)	1.0	0	43.7	1.01
	Ni-Al ₂ O ₃ (F)	1.0	0	76.0	21.0
Sakai <i>et al.</i> ¹⁶⁾	Ni-SiO ₂	0.02-0.05	0.5-0.6	63.0	-
Tokunaga <i>et al.</i> ²¹⁾	Ni-Al ₂ O ₃	0.6	0.3	92.4	-
Rostrup-Nielsen and Hansen ¹⁴⁾	Ni-MgO	1.0	0	-	-

$$*) r_{\text{CH}_4} = k p_{\text{CH}_4}^m p_{\text{CO}_2}^n \quad **) k = k_0 \exp \{-E/(R_g T)\}$$

could be generated from CO₂ when steam was replaced by CO₂¹⁴⁾. It is suggested that dissociated oxygen could be supplied both from the catalyst metal and the support^{1, 11, 13, 15)}. The effect of CO adsorption on the catalyst metal has also been discussed. This adsorption would be more likely to change the reaction rate for several of the metals than the effect of the CO₂ dissociation step¹⁴⁾. In this study, Ni was fixed as the catalyst component and the support was changed. In this case, the effect of CO adsorption would be almost constant as when Ni was used as catalyst component but the CO₂ dissociation step could be influenced by the nature of support. Since CO₂ is well known as an acid gas, adsorption or dissociation of CO₂ may be improved with a basic catalyst. Alumina might be basic nature but SiO₂ might not be so²⁰⁾. The effect of MgO addition to SiO₂ has been reported^{9, 10)}. The basicity of the MgO-SiO₂ catalyst increases with MgO content while maximum acidity is attained at 50mol%. The maximum value of acidity is lower by about one-tenth than that of basicity. Catalytic activity in the hydrogen transfer reaction was well correlated with basicity⁹⁾. We can then conclude that the basicity of Al₂O₃ (catalyst B,E,F) and SiO₂ with MgO (catalyst A) will increase the overall basicity of supported Ni catalysts and activate CO₂. On the other hand, the neutral or acid nature of SiO₂ (catalyst C,D,G) can not activate CO₂. These discussions, based on acid-base properties of the catalyst, can explain the effect of supports as shown in Fig.2. The catalytic activity varied depending on the type of support according to the following order, Al₂O₃ > SiO₂ with MgO > SiO₂. This agrees with the effect of supports in the case of CO₂ hydrogenation¹⁸⁾ in which the activation of CO₂ is also important.

Conclusions

Carbon dioxide reforming of CH₄ over several kinds of supported Ni catalysts has been investigated. The catalytic activity depends to a large extent on the kind of support. Among the various supports, Al₂O₃ showed higher activities than SiO₂. Alumina-supported catalysts also had stable activities. The addition of MgO to SiO₂-supported catalyst increased catalytic activity but decreased stability.

The rate equation was expressed in terms of the

partial pressures of CH₄ and CO₂. Various dependencies on the partial pressure of CH₄ and CO₂ were observed. Selection of the support was an important factor since basicity of the support was assumed to activate CO₂.

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Nomenclature

E	= activation energy	[kJ/mol]
$F_{\text{CH}_4,0}$	= feed gas flow rate of CH ₄	[mol/s]
k	= rate constant	[mol/(Pa ^m ·s·kg-cat)]
k_0	= frequency factor in Arrhenius equation	[mol/(Pa ^m ·s·kg-cat)]
m	= reaction order with respect to CH ₄	[-]
n	= reaction order with respect to CO ₂	[-]
r_{CH_4}	= reaction rate of CH ₄	[mol/(s·kg-cat)]
R_g	= gas constant	[J/(mol·K)]
p_{CH_4}	= partial pressure of CH ₄	[Pa]
p_{CO_2}	= partial pressure of CO ₂	[Pa]
T	= reaction temperature	[K]
W	= catalyst weight	[kg]
X_{CH_4}	= conversion of CH ₄	[-]

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