ผลกระทบของไฮโดรเจนซัลไฟด์ คาร์บอนไดออกไซด์ และ ออกซิเจน ต่อกระบวนการรีฟอร์มมิ่งมีเทนด้วยไอน้ำ บนตัวเร่งปฏิกิริยา Ni/CeO_2 และ Ni/Al_2O_3

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บทคัดย่อ

งานวิจัยนี้ทำการศึกษาอิทธิพลของก๊าซไฮโดรเจนซัลไฟด์และคาร์บอนไดออกไซด์ ต่อกระบวนการผลิตไฮโดรเจน ด้วยวิธีรีฟอร์มมิ่งมีเทน โดยใช้ตัวเร่งปฏิกิริยา Ni/CeO_2 และ Ni/Al_2O_3 จากการทดลองพบว่าทั้งก๊าซไฮโดรเจนซัลไฟด์ และคาร์บอนไดออกไซด์ มีส่วนยับยั้งอัตราการเกิดกระบวนการรีฟอร์มมิ่ง ซึ่งส่งผลให้สัดส่วนของไฮโดรเจนสุดท้ายลดลง ทั้งนี้การที่มีไฮโดรเจนซัลไฟด์อยู่ในระบบ 2-10 ppm จะทำให้อัตราการเกิดปฏิกิริยาลดลงอย่างรวดเร็วเนื่องมาจากการ เกิดกระบวนการซัลฟิเดชั่น   และการเสื่อมสภาพนี้ไม่สามารถสามารถกลับคืนได้สมบูรณ์ถึงแม้ว่าจะมีการกำจัด ไฮโดรเจนซัลไฟด์ ออกจากระบบแล้วก็ตาม ทั้งนี้ทั้งนั้นหากเทียบภายใต้สภาวะเดียวกันแล้วจะพบว่า Ni/CeO_2 จะมีความ สามารถในการต้านทานการเสื่อมสภาพได้ดีกว่า Ni/Al_2O_3การเสื่อมสภาพเช่นนี้เช่นเดียวกับที่พบในก๊าซคาร์บอนไดออกไซด์ เนื่องด้วยคาร์บอนไดออกไซด์จะไปยับยั้งการดูดซับมีเทนและไอน้ำ การที่มีก๊าซคาร์บอนไดออกไซด์อยู่ในระบบจึงส่งผล ด้านลบต่อกระบวนการรีฟอร์มมิ่งมีเทนด้วยไอน้ำทั้งในตัวเร่งปฏิกิริยาทั้งสองประเภท นอกจากนี้ยังได้ลองทำการเติมก๊าซ ออกซิเจนผ่านทางท่อขนาดเล็กลงไป   ซึ่งทำให้กระบวนการนี้คล้ายกับการรีฟอร์มมิ่งแบบออโต้เทอร์มอลรีฟอร์มมิ่ง ออกซิเจนจะช่วยส่งเสริมอัตราการเกิดกระบวนการรีฟอร์มมิ่งมีเทนด้วยไอน้ำในตัวเร่งปฏิกิริยาทั้งสองประเภท ถึงแม้ว่า ปริมาณการผลิตไฮโดรเจนจะลดลงตามการเพิ่มปริมาณออกซิเจน เนื่องด้วยออกซิเจนจะไปยับยั้งการดูดซับไอน้ำ และ เป็นผลจากเกิดปฏิกิริยาออกซิเดชั่นกับไฮโดรเจนในระบบ

คำสำคัญ : ไฮโดรเจนซัลไฟด์ / ไฮโดรเจน / กระบวนการรีฟอร์มมิ่งมีเทนด้วยไอน้ำ / ออโต้เทอร์มอลรีฟอร์มมิ่ง / เซลล์เชื้อเพลิง

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Effects of H_2S, CO_2, and O_2 on Catalytic Methane Steam Reforming over Ni/CeO_2 and Ni/Al_2O_3 Catalysts

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Abstract

In the present work, the influences of H_2S and CO_2 on hydrogen production from methane steam reforming reaction over Ni/CeO_2 and Ni/Al_2O_3 were studied. According to the experiment, both H_2S and CO_2 inhibited the methane steam reforming rate over both catalysts and consequently resulted in the decreasing of hydrogen production yield. In the presence of H_2S (2-10 ppm), the rate dramatically decreased due to the sulphidation and cannot be fully recovery even though H_2S is removed from the feed. At the same operating conditions, Ni/CeO_2 provided higher resistance toward the deactivation than Ni/Al_2O_3. CO_2 also presented negative effect on the production of hydrogen from methane steam reforming over both catalysts due to the inhibition of methane and steam adsorption by CO_2. The adding of oxygen through the inlet feed along with methane and steam as the autothermal reforming was also carried out. Oxygen promoted methane steam reforming rate for both catalysts. However, H_2 production from methane steam reforming decreased with increasing oxygen partial pressure.

Keywords : H_2S / Hydrogen / Methane Steam Reforming / Autothermal Reforming / Fuel Cell

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1. Introduction

Nowadays, most of the energy resources come from oil which the price is raising and it appears to be in the shortest supply worldwide. Hydrogen is expected to be an important alternative energy resource in the near future. In order to produce hydrogen, the catalytic reforming reactions have always been applied [1, 2]. By these reactions, the hydrocarbon elements such as methane can be reformed by the oxidants such as steam [3], oxygen [4-7], or carbon dioxide [8] and released hydrogen as presented in the reactions below:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H = 206.2 \text{ kJ/mol} \qquad \textbf{(1)}$$
$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H = 247 \text{ kJ/mol} \qquad \textbf{(2)}$$
$$CH_4 + {}^1\!/_2O_2 \rightarrow CO + 2H_2 \qquad \Delta H = -22.6 \text{ kJ/mol} \qquad \textbf{(3)}$$
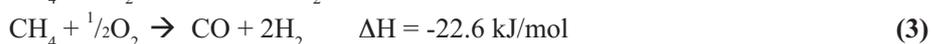
Currently, the commercial process for hydrogen production is based on the steam reforming reaction. In recent years, many researchers have also investigated the combination between the steam reforming with the partial oxidation reaction in a single process, calling an autothermal reforming. By this combination, exothermic heat from the partial oxidation can directly supply the energy for the endothermic steam reforming reaction. Therefore, it is considered to be thermally self-sustaining and consequently more economical than steam reforming. The main disadvantage of this reaction is the lower synthesis gas (H_2 and CO) produced from this reaction compared to steam reforming.

Several types of catalysts can be used to activate these reactions. The important properties for the reforming catalyst are its activity toward reforming reaction, and its resistance toward carbon formation [9]. The catalyst should have high thermal stability in order to maintain the reforming activity under the process conditions. In addition, the reforming catalyst should also have high resistant toward deactivation from poisoning. The major reason in rapid decreasing of the reforming activity is due to poisons, which is defined as components in the reactant or product from the reaction. The poisoning of catalyst could be separated into three groups. These are the poisons to the intrinsic activity, the poison to the activity of the single pellet, and the poison to the performance of the whole reactor [9]. If the active surface sites of the catalyst are blocked by chemical components such as carbon atoms, sulphur or alkali compounds, this phenomenon is called fouling. It leads to the decline in activity of the catalyst. However, the activity of the catalyst could be regained when these compounds are removed from the flow, if the strength of the adsorption bond is not strong [9]. Hydrogen sulphide (H_2S) is the stable chemical compound that has been reported to poisonous for reforming catalysts. In the experimental scale, the reforming feed is normally desulphurized to a level below 0.2 ppm [9]. As chemisorption of hydrogen sulphide on the catalyst surface is reversible, it is then possible to remove sulphur from the catalyst simply by decreasing the sulphur content of the feed. This might be achieved in experiments using a high flow rate where the diffusion restriction does not occur [10]. However, in the industrial level, this method normally results in a slow regeneration [11].

Nowadays, natural gas and biogas are known as the major possible feedstock for hydrogen produc-

tion due to their economic availability. Methane is the major component for both natural gas and biogas. However, both gases also consist of some poisonous compounds such as H_2S in the trace quantity and CO_2 varied from 5% to 40%. The composition of Thailand natural gas and biogas are presented in the Table 1.

Table 1 Composition of natural gas and biogas

Compounds	Natural gas (%)	Biogas (%)
Methane (CH_4)	67.4	55-60
Ethane (C_2H_6)	9.3	-
Propane (C_2H_8)	5.1	-
Other Hydrocarbons	2 to 3	-
Carbon Dioxide (CO_2)	14.3	39-44
Nitrogen	1.09	-
Water Vapour	Trace	-
Hydrogen Sulfide	0.02	< 1

In the present work, the influences of H_2S and CO_2 appearance in the gas on the hydrogen production from methane steam reforming reaction were studied. Moreover, the adding of oxygen through the inlet feed along with methane and steam as the autothermal reforming was also carried out in order to compare the performance with the conventional steam reforming. Ni/CeO_2, which has been widely reported to provide high resistance toward carbon formation [12, 13], was selected as the reforming catalyst in this study. For comparison, Ni/Al_2O_3 was also used as the reforming catalyst, according to the economical point of view.

2. Experimental

2.1 Material preparation

Ni/CeO_2 and $Ni/\alpha-Al_2O_3$ were prepared by impregnating the support (CeO_2 and $\alpha-Al_2O_3$) with $NiCl_3$ (from Alfa) solution at room temperature. This solution was stirred by magnetic stirring (100 rpm) for 6 hours. The solution was then dried overnight in an oven at 110°C, and calcined in air at 1,000°C for 6 hours. The catalysts were also reduced with 5% hydrogen in helium at 300°C for 6 hours before testing the steam reforming.

2.2 Experimental set-up

Fig. 1 shows the schematic diagram of the experimental reactor system. It consists of three main sections: feed, reaction, and analysis sections. The main obligation of the feed section is to supply the components of interest such as CH_4, H_2O, H_2S, CO_2, or O_2 to the reaction section, where an 8-mm internal diameter and 40-cm length quartz reactor was mounted vertically inside a furnace. The catalyst was loaded in the quartz reactor, which was already packed with a small amount of quartz wool to prevent the catalyst from moving. The residence time was kept constant at 5×10^{-4} g min cm^{-3}. The weight of catalyst loading was 10-100 mg, while a

typical range of total gas flow was 20-200 ml/min depending on the desired gas velocity. The gas mixture was flowed though the catalyst bed in the quartz reactor. A type-K thermocouple was inserted into the annular space between the reactor and the

furnace. The thermocouple was mounted on the reactor in close contact with the catalyst bed to minimize the temperature difference between the catalyst bed and the thermocouple.
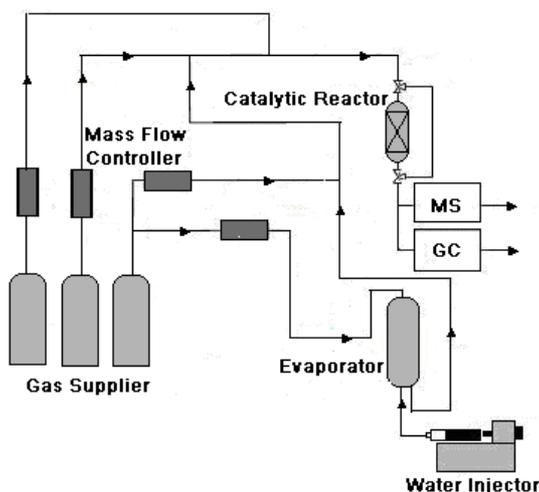
Fig. 1 The reactor system in this research

The exit gas was transferred via trace-heated lines to the analysis section, which consists of a Porapak Q column Shimadzu 14B gas chromatography (GC) and a mass spectrometer (MS). The gas chromatography was applied in order to investigate the steady state condition experiments, whereas the mass spectrometer was used for the transient and H_2S experiments. The mass spectrometer was applied in order to investigate the effect of O_2 partial pressure on the steam reforming rate. In the present work, the outlet of the GC column was directly connected to a thermal conductivity detector (TCD). In order to satisfactorily separate CH_4, CO, CO_2, and H_2O, the temperature setting inside the GC column was programmed varying with time. In the first 3 min, the column temperature was constant at 60°C. Then, it was increased steadily by

the rate of 15°C per min until 120°C. Finally, the temperature was decreased to 60°C.

3. Results and Discussions

3.1 Methane steam reforming in the presence of H_2S

In order to study the influence of H_2S on methane steam reforming rate, the investigation was carried out with 0.03 atm methane and 0.05 atm steam, and addition of H_2S in N_2 to give an inlet concentration of 10 ppm. The rate of reaction was calculated based on the mole of methane conversion per units of catalyst (kg) and time (hr); mol/kg.hr.

Catalysts were heated up slowly in helium to 900°C. At the isothermal condition, methane/steam/helium gas mixture was introduced. H_2

production from methane steam reforming was observed. When methane steam reforming rate reached steady state, 10 ppm H_2S in N_2 was added into the system. H_2 production from this reaction in the presence of H_2S was compared to that without H_2S. After 60 min, H_2S was then switched off, and methane steam reforming rate after H_2S removal was also investigated. The effect of H_2S on the productions of CO_2 and H_2 from methane steam reforming over Ni/Al_2O_2, and Ni/CeO_2 is shown in Fig. 2.
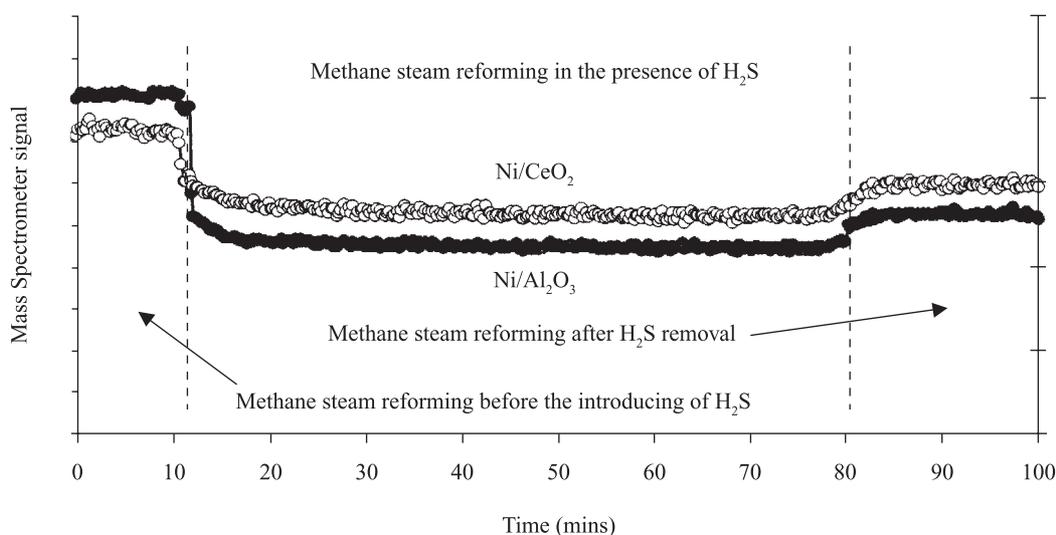
Fig. 2 Influence of H_2S (10 ppm) on methane steam reforming rate over Ni/Al$_2$O$_3$ and Ni/CeO$_2$ at 900°C

H_2 production over both materials decreased dramatically when H_2S was introduced, especially for Ni/Al$_2$O$_3$. After switched off the H_2S line, H_2 productions slightly increased. In the presence of H_2S, the changing in methane steam reforming rate for all catalysts could be due to the sulphidation on the surface of these materials. After exposure in CH$_4$/ H$_2$O/H$_2$S/He gas mixture for 1 hour (period 2), the analysis of the degree of sulphiding was carried out by XPS. The degree of sulphiding on the surface of these materials was compared with that of the same material after re-exposure in CH$_4$/H$_2$O/He gas mixture for 1 hour (period 3) in order to investigate whether sulphur can be removed from the surface of material by steam reforming. These results (S/Ni) are presented in Table 2.

Table 2 Sulphidation of catalysts after exposure in steam reforming in the presence of H_2S for 1 hour, and re-exposure in steam reforming without H_2S for 1 hour; 0.03 atm CH_4, 0.05 atm H_2O, and 10 ppm H_2S

Catalyst	Atomic Ratio (S/Ni) after period 2	Atomic Ratio (S/Ni) after period 3
Ni/Al_2O_3	2.63	2.61
Ni/CeO_2	1.97	1.90

The degree of sulphiding over both catalysts slightly decreased after re-exposure in $CH_4/H_2O/He$ gas mixture indicated the low sulphur removal from the surface. Table 3 presents methane steam reforming rates over these materials in the presence and after removal of H_2S. According to these tables, Periods 1, 2, and 3 refer to methane steam reforming without H_2S, steam reforming in the presence of H_2S, and steam reforming after H_2S removal respectively.

Table 3 Steam reforming rate in the presence and after removal of H_2S at 900°C using 0.03 atm CH_4, 0.05 atm H_2O, and 1,500 ppm H_2S

Catalyst	Steam reforming rate (mol/kg.hr)		
	Period 1	Period 2	Period 3
Ni/Al_2O_3	110	21.1	25.3
Ni/CeO_2	103	33.4	42.1

In order to investigate the effect of inlet H_2S partial pressure on methane steam reforming, different inlet H_2S partial pressures (2, 4, 6, and 8 ppm) were introduced in order to investigate the influence of inlet H_2S partial pressure on methane steam reforming rate. Measurement was carried out using 0.03 ppm methane and 0.05 atm steam at 900°C. Table 4 presents the effect of H_2S partial pressure on methane steam reforming rate. Methane steam reforming rate decreased with increasing H_2S partial pressure for both catalysts. According to the result in this table, Ni/CeO_2 provides higher resistance toward the sulphidation compared to Ni/Al_2O_3.

Table 4 Effect of inlet H_2S partial pressure on the steam reforming rate
at 900°C (0.03 atm CH_4, and 0.05 atm H_2O)

Catalyst	Steam reforming rate (mol/kg.hr) at different inlet H_2S concentration			
	2 ppm	4 ppm	6 ppm	8 ppm
Ni/Al_2O_3	73.4	58.7	42.2	33.8
Ni/CeO_2	92.1	78.4	55.9	42.9

3.2 Methane steam reforming in the presence of CO_2

Methane steam reforming in the presence of carbon dioxide for both catalysts was investigated by adding different inlet carbon dioxide partial pressures to the feed gas at several operating temperatures. The inlet carbon dioxide partial pressure was added from 0.02 atm to 0.08 atm, while the inlet methane and steam partial pressure were kept constant at 0.03 atm and 0.05 atm respectively. Carbon dioxide presented negative effect on methane steam reforming rate over both catalysts as shown in Fig. 3.

Although this component increased the yield of CO production from methane steam reforming, it presented negative effect on H_2 production in the range of conditions studied.
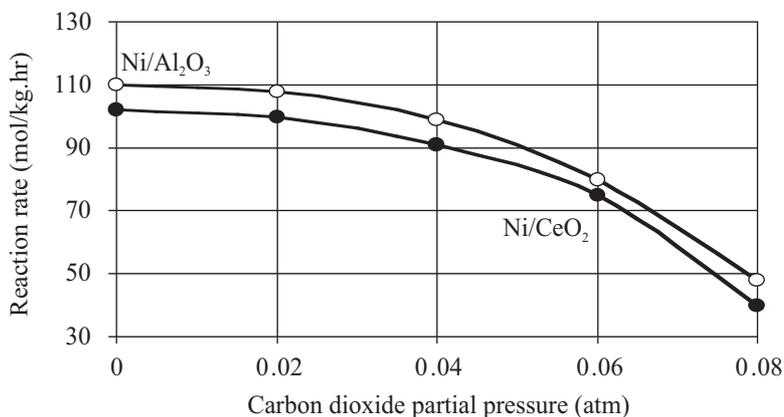
Fig. 3 Effect of CO_2 on methane steam reforming rate (mol of methane conversion per unit time) over Ni/Al_2O_3 and Ni/CeO_2 at 900°C

The influence of carbon dioxide on the rate of methane conversion was developed as presented below [12]. This rate isotherm is developed in order to predict the effect of carbon dioxide on the performance of catalyst toward methane steam reforming reaction, as carbon dioxide always accumulate along with methane and stem in the large scale reforming system.

$$\text{Rate}_{\text{total}} = \text{Rate}_{(\text{without } CO_2)} - \text{Rate}_{(\text{due to the influence of } CO_2)}$$

$$\text{Rate}_{\text{total}} = kP_{CH_4}P_{H_2O} - k''(P_{CO_2})^m$$

$$\frac{\text{Rate}_{\text{total}}}{\text{Rate}_{SR}} = 1 - \left(\frac{k''}{kP_{CH_4}P_{H_2O}}\right)(P_{CO_2})^m$$

Therefore, $\quad \dfrac{Rate(x\%CO_2)}{Rate(0\%CO_2)} = 1 - B(P_{CO_2})^m$

Where Rate($x\%CO_2$) is the rate of methane conversion at different carbon dioxide partial pressure (x). Table 5 presents the mean values of both parameters (B, and m) for each catalyst in the range of conditions studied.

Table 5 The mean values of both parameters

Temperature (°C)	Mean values of B and m for Ni/Al$_2$O$_3$	
	B	m
825	3.71	0.73
850	4.62	0.81
875	5.59	0.89
900	6.52	0.98
Temperature (°C)	Mean values of B and m for Ni/CeO$_2$	
	B	m
825	3.14	0.72
850	4.43	0.79
875	5.41	0.89
900	6.49	0.95

The addition of carbon dioxide together with methane/steam gas mixture reduced methane steam reforming rate due to the adsorption of carbon dioxide on the metal surface (Ni*) in reaction (4) below [12].

$$CO_2 + Ni^* \Leftrightarrow CO + Ni\text{-}O \quad \textbf{(4)}$$

From the reaction, carbon dioxide reacts with the catalyst active site (Ni*) rapidly and results in the inhibition of the methane adsorption. Similarly, H$_2$ production decreased with increasing carbon dioxide partial pressure due to the inhibition of steam adsorption by carbon dioxide.

3.3 Methane steam reforming in the presence of O$_2$

Methane steam reforming in the presence of oxygen was studied by adding of different oxygen partial pressures into the feed gas at several operating temperatures. The effect of oxygen on the steam reforming rate, and each component production (CO, CO$_2$, and H$_2$) were observed. Furthermore, a rate coefficient based on the conversion of me-

thane from methane steam reforming in the presence of oxygen was also developed in order to predict the effect of oxygen on the catalyst performance in the large scale reforming system.

In order to investigate the effect of oxygen on methane steam reforming rate, the inlet methane and steam partial pressure were kept constant at 0.03 and 0.05 atm respectively, while the inlet oxygen partial pressure was varied from 0 to 0.04 atm. At steady state, methane steam reforming rate in the presence of different oxygen partial pressures was observed as presented in Table 6.

Table 6 Methane steam reforming rate (mol of methane conversion per unit time; mol/kg.hr) in the presence of oxygen (0.03 atm CH_4 and 0.05 atm H_2O)

Temp. (°C)	Steam reforming rate of Ni/Al$_2$O$_3$ (mol/kg.hr) at different inlet O$_2$ partial pressures (atm)				
	0.00	0.01	0.02	0.03	0.04
825	83	121	143	166	184
850	85	146	164	181	202
875	97	162	180	199	219
900	110	188	201	218	227
Temp. (°C)	Steam reforming rate of Ni/CeO$_2$ (mol/kg.hr) at different inlet O$_2$ partial pressures (atm)				
	0.00	0.01	0.02	0.03	0.04
825	69	111	132	157	171
850	80	135	151	174	192
875	93	150	169	190	202
900	103	164	183	198	209

Methane steam reforming rate for both materials increased with increasing inlet oxygen partial pressure. However, oxygen presented negative effect on the CO production, and also presented negative effect on H_2 production from methane steam reforming over Ni/Al$_2$O$_3$, and Ni/CeO$_2$. Fig. 4 and 5 show the effect of oxygen on the hydrogen and CO/CO$_2$ production ratio. It should be noted that hydrogen production in Fig. 4 is represented in term of relative hydrogen production (hydrogen production in the presence of oxygen/ hydrogen production without oxygen). Clearly both hydrogen production and CO/CO$_2$ ratio decreased with increasing oxygen partial pressure in the range of conditions studied. Oxygen adsorbs on the surface of metal catalyst and produces the oxidized state, Ni-O, via reaction (5) below [12].

$$O_2 + 2Ni^* \rightarrow 2Ni\text{-}O \qquad (5)$$

The increasing of methane conversion and CO_2 production could be due to the promotion of C and CO oxidation by this component, which conse-quently resulted in the decreasing of CO produc-tion. H_2 production decreased with increasing oxygen partial pressure due to the inhibition of steam adsorption by this component and the oxidation of hydrogen production by oxygen atom [12].
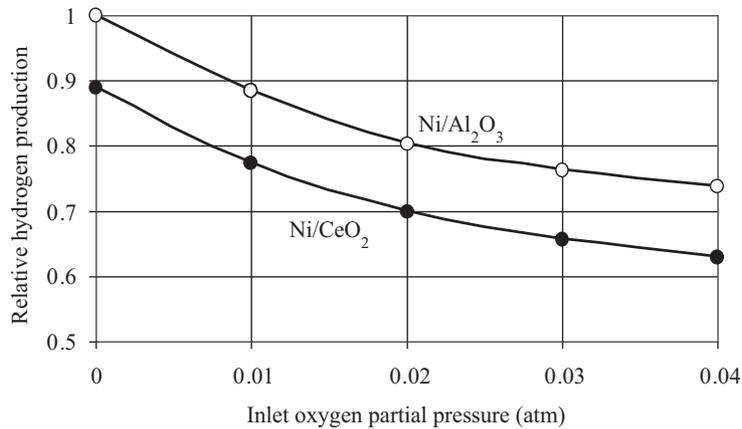
Fig. 4 Effect of O_2 on the rate of hydrogen production over Ni/Al_2O_3 and Ni/CeO_2 at 900°C
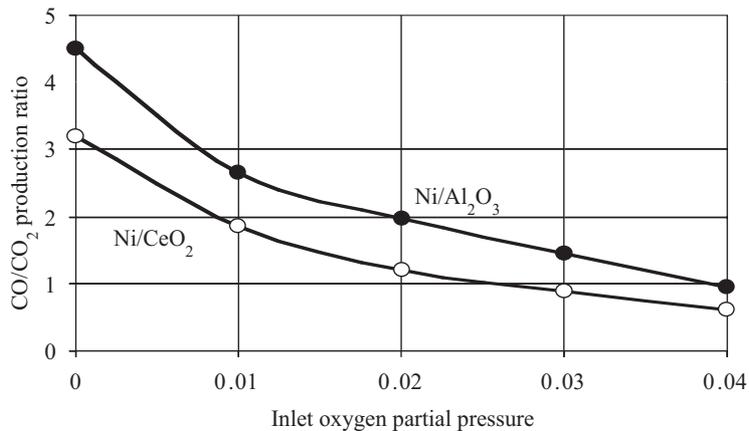
Fig. 5 Effect of O_2 on the CO/CO_2 production ratio from methane steam reforming at 900°C

In order to compare the influence of oxy-gen on the rate of methane conversion over each catalyst, the simple relative rate coefficient was developed [12]. This coefficient was based on the assumption that the total rate of methane conver-sion is the combination between the rate of steam reforming and the rate due to the influence of O_2 as presented:

$$\text{Rate}_{total} = \text{Rate}_{\text{steam reforming(SR)}} + \text{Rate}_{(\text{due to the influence of } O_2)}$$

$$\text{Rate}_{total} = kP_{CH_4}P_{H_2O} - k'(P_{CO_2})^n$$

$$\frac{\text{Rate}_{total}}{\text{Rate}_{SR}} = 1 - \left(\frac{k'}{kP_{CH_4}P_{H_2O}}\right)(P_{O_2})^n$$

$$\text{Therefore,} \quad \frac{\text{Rate}(x\%O_2)}{\text{Rate}(0\%O_2)} = 1 - A(P_{O_2})^n$$

Where rate ($x\%\ O_2$) is the rate of methane conversion at different oxygen partial pressures (x). Table 7 presents the mean values of both parameters (A, and n) for each catalyst in the range of conditions studied.

Table 7 The mean values of all parameters

Temperature (°C)	Mean values of A and n for Ni/Al$_2$O$_3$	
	A	n
825	5.60	0.61
850	3.50	0.54
875	1.89	0.42
900	0.94	0.30
Temperature (°C)	Mean values of A and n for Ni/CeO$_2$	
	A	n
825	5.95	0.58
850	3.97	0.52
875	1.82	0.39
900	1.12	0.27

4. Conclusion

Methane steam reforming rate in the presence of H_2S (2-10 ppm) dramatically decreased and cannot be fully recovery over both Ni/Al$_2$O$_3$ and Ni/CeO$_2$ even though H_2S is removed from the feed. At the same operating conditions, Ni/CeO$_2$ provided higher resistance toward the deactivation due to the sulphidation. The presence of CO_2 in the feed also inhibited the production of hydrogen from methane steam reforming, which was proven to be due to the inhibition of methane and steam adsorption by CO_2 [12]. Consequently, the removal of both CO_2 and H_2S might be required in order to maximize the yield of hydrogen production from methane steam reforming.

The addition of oxygen together with methane/steam gas mixture, as the autothermal reforming, was observed to increase methane steam reforming rate for both catalysts. However, H_2 production from methane steam reforming decreased with increasing oxygen partial pressure due to the inhibition of steam adsorption by this component and the oxidation of hydrogen production by oxygen atom [12].

5. References

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