Effect of Nickel Particle Size on Dry Reforming Temperature

M. Chareonpanich, N. Teabpinyok, and S. Kaewtaweesub

***Abstract*—The effect of nickel particle sizes of Ni/Al_2O_3 catalysts on the performance of synthesis gas production via dry reforming reaction of methane and carbon dioxide was investigated. Various nickel particle sizes were prepared by using solvothermal, hydrothermal and impregnation methods. The particle sizes of nickel metal on Al_2O_3 support were examined by Transmission Electron Microscopy (TEM). It was found that the nickel particle sizes obtained from the solvothermal method were in the range of 5-10 nm. When the hydrothermal method was applied, the rod-shape nickel particles in the length of 12-15 nm, 16-20 nm and 30-35 nm were synthesized with the time periods of 5, 10, and 15 h, respectively. The obtained Ni/Al_2O_3 catalysts were tested for dry reforming reaction in a fixed bed reactor at 450-750°C. It was found that the nickel metal of 5-10 nm particle size obtained from the solvothermal method revealed the highest methane and carbon dioxide conversions in all ranges of reaction temperatures. At 750 °C, the maximum conversion was obtained (83 % for CH_4 and 55 % for CO_2) and CO and H_2 yields were 48 % and 52 %, respectively.**

***Index Terms*—Nickel particle size, Synthesis gas production, Dry reforming, Methane, Carbon dioxide.**

I. INTRODUCTION

As the increasing demand for high quality and environmentally friendly transportation fuels, the Gas-to-liquid (GTL) process has attracted much interest as a promising technology to meet the world's energy needs [1]-[3]. The GTL process with synthesis gas as a potential source of hydrocarbon synthesis is more interesting in an industrial scale since liquid fuel products offer significant ecological and efficient benefits over those fuels derived from crude oil [4]-[6].

The GTL process [7] is composed of two parts; one is the synthesis gas generation from natural gas, and the other is synthesis gas conversion to liquid fuels. Synthesis gas can be produced from methane mainly by steam reforming but have limitations, like high energy requirements and high H_2/CO ratio. It is produced by the non-catalytic partial oxidation reaction which is mildly exothermic but operates at very severe conditions. The liquid fuels produced via FTS have high cetane number, low contents of sulfur and aromatics, of which makes this process environmentally friendly for gasoline and diesel engines production [8].

Recently, much effort has been devoted to carbon dioxide reforming of methane (dry reforming) to produce synthesis gas in the presence of catalysts. According to this purpose, nickel supported alumina catalysts have been much utilized [9]-[12].

In this present research, the aim to reduce high energy requirements for the synthesis gas production from carbon dioxide and methane via dry reforming reaction has been focused. Nickel metal s of various particle sizes were prepared by using solvothermal, hydrothermal, and impregnation methods and characterized by Transmission Electron Microscopy (TEM), N_2 sorption analysis, and X-ray fluorescence (XRF) analyzer. The effect of nickel particle size on the performance of synthesis gas production at the temperature ranges of 450-750°C was investigated.

II. EXPERIMENTAL

A. *Preparation of catalysts*

A commercial alumina (Fluka, 100 % purity) was used as a catalyst support in the reforming reaction. The nickel nitrate salt ($Ni(NO_3)_3 \cdot 6H_2O$, Univar, 97.0 % purity) was used as a metal precursor. In each experiment, nickel metal of 5 wt.% was loaded on alumina by using 3 different methods including wet impregnation method, solvothermal method, and hydrothermal method.

For the wet impregnation method, a required amount of an aqueous solution of nickel was mixed with alumina powder. The mixture was agitated at room temperature for 1 h and dried at 120 °C for 24 h. The dried product was calcined in air at 550 °C for 4 h.

For the solvothermal method, nickel nitrate was mixed with 25, 50, 75, and 100% of tetrahydrofuran (THF) in water and then added into alumina powder. The mixture was agitated at room temperature for 1 h and dried at 120 °C for 24 h. The dried product was calcined in air at 550 °C for 4 h.

For the hydrothermal method, nickel chloride ($NiCl_2$) was mixed with alumina powder in 3 ml of 10 M NaOH solution, 1 ml of 30% hydrazine solution and 2 ml of distilled water. The mixture was agitated at room temperature for 1 h and hydrothermal treated at 100 °C for 5, 10, and 15 h. The solid products were filtered, washed with distilled water, dried at 120 °C for 24 h, and calcined in air at 550 °C for 4 h.

B. *Characterization of supports and catalysts*

TEM micrographs were obtained by JEOL, JEM-2010 microscope operating from 120 to 200 kV. Prior to analysis,

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the solid catalyst powders were dispersed in acetone and dropped on a copper grid support.

Nitrogen adsorption properties of supports and catalyst were measured using a N_2-adsorption apparatus (Quantachrome, Autosorb-1). Prior to each adsorption-desorption measurement, the sample was out gassed at 300 ^{o}C for 5 h. The surface areas of supports and catalysts were determined by the BET method. The total pore volume (TPV) was calculated from the amount of vapor adsorbed at a relative pressure (P/P_0) closed to unity, where P and P_0 are the measured and equilibrium pressures, respectively.

The chemical compositions of Ni/Al_2O_3 catalysts were measured by XRF analyzer (HORIBA, MESA-500W). The XRF analysis confirms the desired amount of active metals on catalyst supports.

C. *Catalytic performance and product analysis*

In order to perform the catalytic performance testing, the Ni/Al_2O_3 catalysts were placed in the reforming reactor (Inconel tube, outer diameter of 3/8 inch) with the bed length of 4 cm.

Prior to the catalytic experiments, the catalysts were in situ calcined in air at 500 ^{o}C for 1 h with the flow rate of 60 ml/min (NTP), flushed with nitrogen and followed by reduction in hydrogen atmosphere at 400 ^{o}C for 6 h with the flow rate of 60 ml/min (NTP), and finally flushed and cooled down in nitrogen atmosphere. After activation, the catalysts were ready for the catalytic performance test.

After reduction, a mixture of carbon dioxide and methane with CO_2/CH_4 molar ratio of 1 was introduced into the reforming reactor where the mixed gases were converted to synthesis gas on the $5Ni/Al_2O_3$ catalyst at the temperature ranges of 450 to 750 ^{o}C, total gas pressure of 1 MPa and total flow rate of 50 ml/min (NTP). The reaction temperature was controlled and measured by a thermocouple inserted into the catalyst bed. The effluent products including H_2, CO, CO_2 and CH_4 were analyzed by gas chromatography equipped with Unibead C columns using a thermal conductivity detector (TCD).

III. RESULTS AND DISCUSSION

A. *Textural properties of catalysts*

The textural properties and particle sizes of nickel metals on alumina obtained from various loading methods are shown in Figs. 1-3.

As shown in the TEM photograph (Fig. 1), the dark spots scattering in the lighter zone reveal the nickel particles and alumina support, respectively. The nickel particle size obtained from the wet impregnation method was significantly large (approximately 100 nm) when compared with other methods.

When the solvothermal method with various percentages of THF in water was applied, the fine spherical particles of nickel with various sizes were obtained (Figs. 2 (a-d)). It can be observed that the particle sizes of nickel ranging between 5 to 10 nm were obtained with 25%, 50% and 75% THF in water, whereas the nickel particles of smaller than 5 nm were obtained with 100% THF. The result implied that THF played an important role as a capping agent [13] and promoted the segregation of nickel particles. However, when water was added in the mixture (25, 50, 75% THF or 75, 50, 25% water), no significant change in nickel particle size was observed.

With the hydrothermal method, nickel metals of spherical and rod-shape particles were obtained, as shown in Figs. 3 (a-c). It can be clearly seen that when the hydrothermal periods were extended from 5 h to 12 h, the nickel metals were gradually transformed from spherical particles to rod-like particles and the particle sizes were also increased with increasing the hydrothermal periods from 5 to 35, respectively.

According to these 3 metal loading methods, the particle sizes of nickel metals obtained from each technique are summarized as shown in Table I.

B. *Sorption isotherms and pore size distribution of catalysts*

The adsorption-desorption isotherms of Ni/Al_2O_3 catalysts obtained from various metal loading techniques are shown in Figs. 4-6. The sorption isotherms of Al_2O_3 and Ni/Al_2O_3 obtained from wet impregnation (Fig. 4) represented Type-V isotherm, indicating the existence of mesoporous structures. It was clearly seen that the specific volume of Ni/Al_2O_3 was rarely reduced after metal loading.

When the solvothermal method was applied (Fig. 5), similar to that of the wet impregnation, Type-V isotherms were observed. However, the broader pore size distribution compared to that of the wet impregnation was clearly seen, this result was contributed to the significant amount of nickel metal incorporating into the structure of Al_2O_3 support as was confirmed by TEM photos in Figs. 2 (c-d).

As shown in Fig. 6, the sorption isotherms of Ni/Al_2O_3 obtained from the hydrothermal loading technique represent Type-V isotherm; however the shifts of isotherms at P/P_0 of 0.6 to 0.76 and 0.95 to 1.0 indicate the existence of both the mesopore and macropore structures.

The BET surface area, mean pore size and total pore volume of all the catalysts prepared from various loading techniques were shown in Table II. The BET surface area of the Ni/Al_2O_3 prepared by solvothermal method was reduced approximately 20 % from that of the fresh Al_2O_3 support due to the incorporation of nickel particles into the support framework, while the mean pore size and total pore volume were hardly changed. However, the different result was observed with the hydrothermal loading technique. This may be attributed to the simultaneous agglomeration and transformation of nickel spherical particles to the rod-shape aggregate particles during the hydrothermal process.

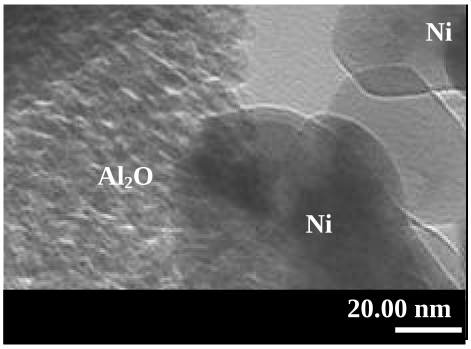

Fig. 1 TEM photo of nickel particle obtained from wet impregnation method.

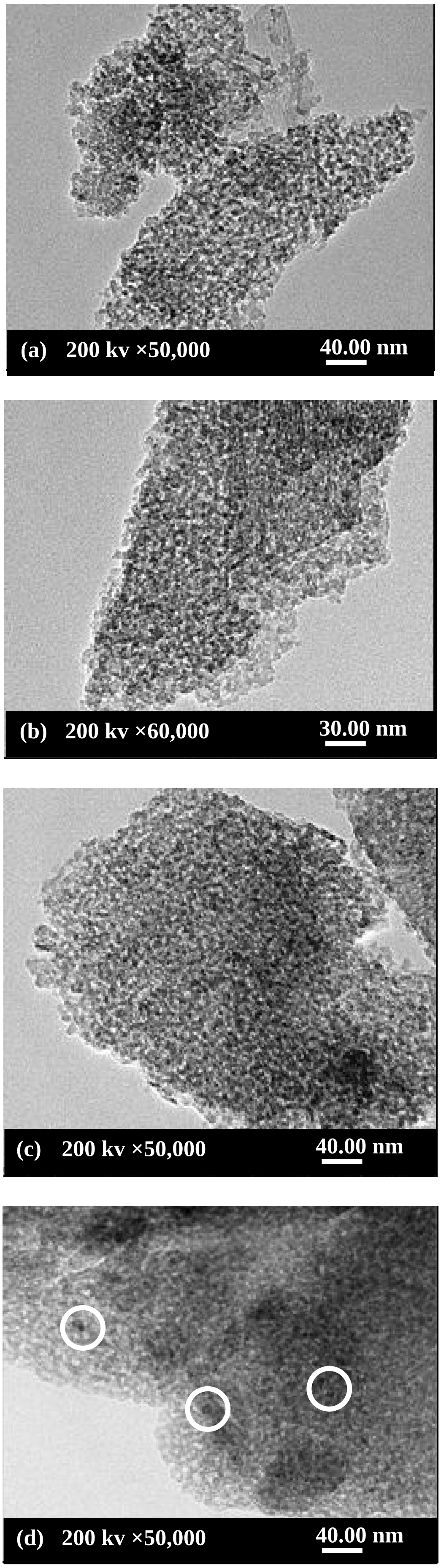

Fig. 2 TEM photos of nickel particles obtained from solvothermal method with (a) 25% (b) 50% (c) 75% (d) 100% of THF in water.

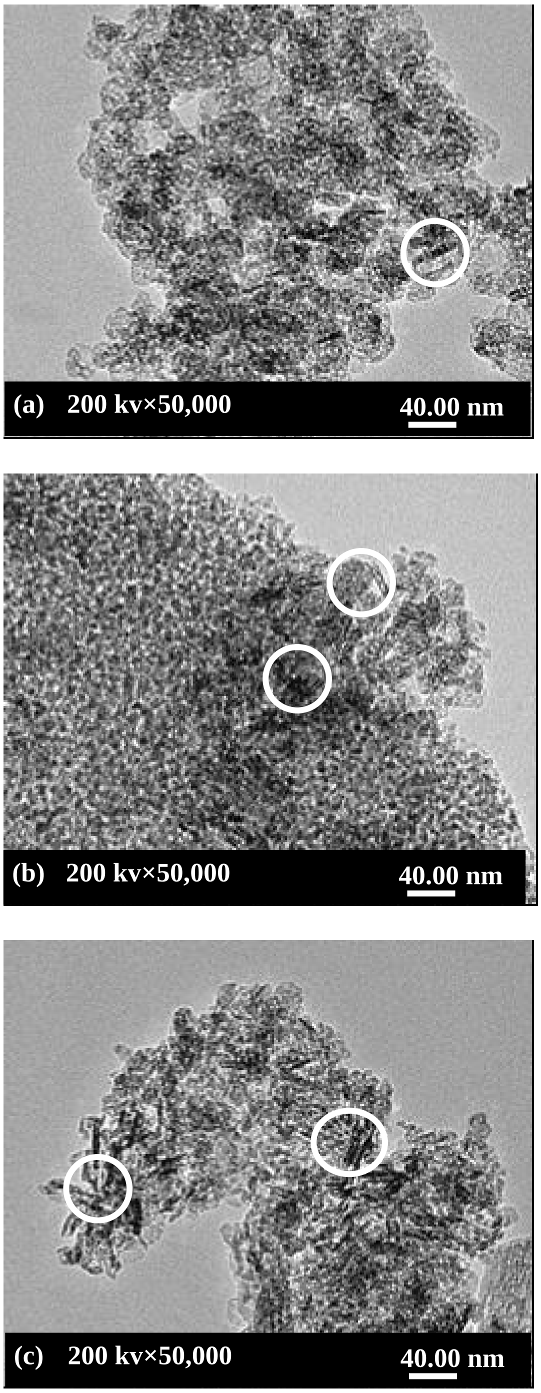

Fig. 3 TEM photos of nickel particles obtained from hydrothermal method at (a) 5 h (b) 10 h (c) 15 h.

Table I Particle sizes of nickel metals obtained from various loading methods

Loading method	Description	Mean particle size (nm)
Wet impregnation	-	200
Solvothermal method	25% THF	5-10
	50% THF	5-10
	75% THF	5-10
	100% THF	> 5
Hydrothermal method	5 h	5-10
	10 h	16-20
	15 h	30-35

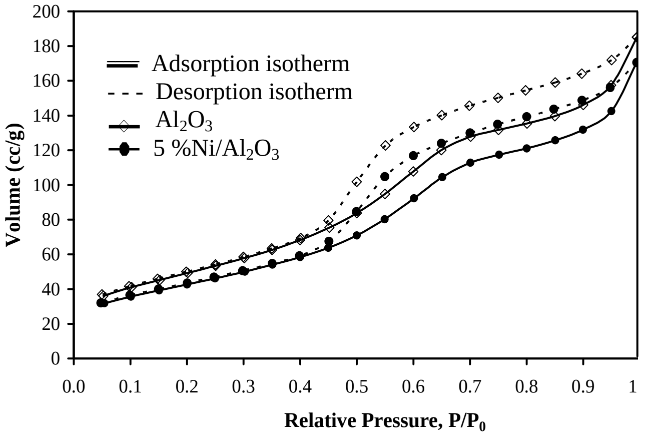

Fig. 4 Sorption isotherms of Al_2O_3 and impregnated 5 wt.% Ni/Al_2O_3.

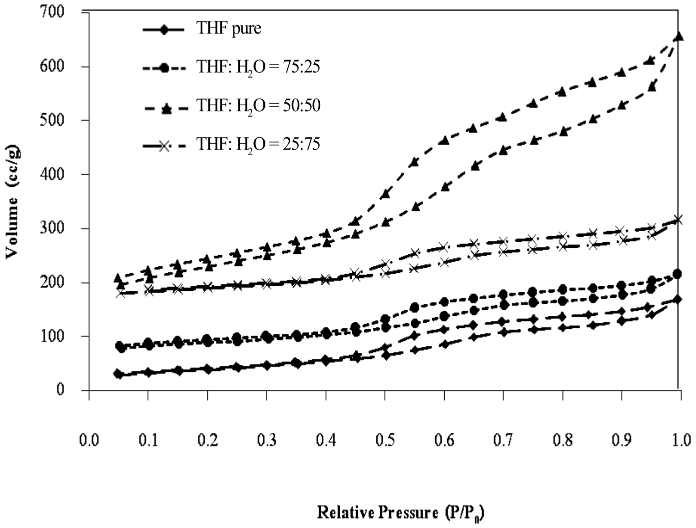

Fig. 5 Sorption isotherms of 5 wt.% Ni/Al_2O_3 prepared by solvothermal method with various THF/H_2O ratios.

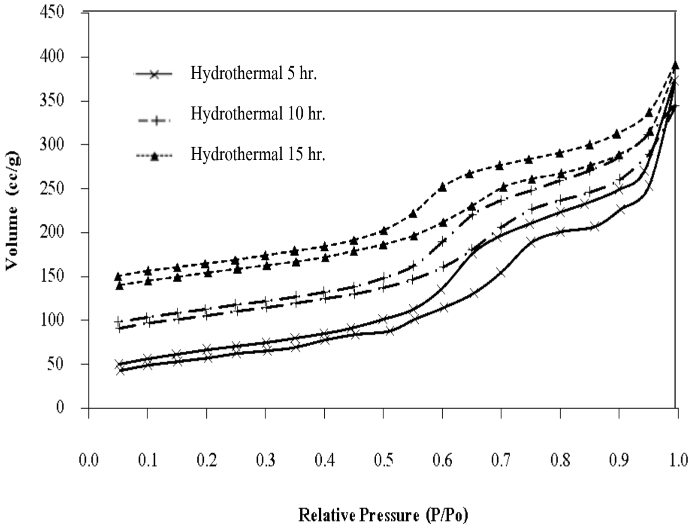

Fig. 6 Sorption isotherms of 5 wt.% Ni/Al_2O_3 prepared by hydrothermal method with various hydrothermal synthesis periods.

Table II Structural properties of nickel metals obtained from various loading methods

Loading method	Description	BET surface area (m^2/g)	Mean pore size (nm)	Total pore volume (cm^3/g)
Al_2O_3	w/o loading	182	7.2	0.29
Wet impregnation	0% THF	157	7.2	0.27
Solvothermal method	25% THF	145	7.1	0.26
	50% THF	149	7.1	0.26
	75% THF	142	7.2	0.25
	100% THF	145	7.2	0.26
Hydrothermal method	5 h	205	11.3	0.58
	10 h	204	9.0	0.46
	15 h	198	9.2	0.46

As a result, the BET surface area, mean pore size and total pore volume of the hydrothermal loaded Ni/Al_2O_3 catalysts were higher than those prepared from other techniques.

C. *Performances of catalysts*

The amounts of nickel metal loaded on Al_2O_3 support were confirmed by the XRF analysis and no significant differences in all cases was observed (4.7 to 5.2 wt.% nickel). The conversions of CH_4 and CO_2 are shown in Table III.

The maximum conversions of both CH_4 and CO_2 are obtained at the reaction temperature of 750 ^oC. The lower temperatures (450 to 700 ^oC) leaded to lower CH_4 and CO_2 conversions and CO selectivity. This was due to the strong endothermic reaction of the dry reforming process (ΔH_{298} = 247 kJ/mol). However, it should be noted that the particle size of nickel metals exhibited a great effect on the dry reforming reaction temperature as it greatly enhanced the CH_4 and CO_2 conversion.

As the particle size of nickel metal decreases, the H_2 uptake and the reduction temperature of nickel oxide to nickel metal might be increased, and therefore the optimum H_2 uptake and the reduction temperature should be again clearly investigated in order to maximize the CH_4 and CO_2 conversion and CO selectivity.

Table III Conversions of CH_4 and CO_2 at the reaction temperature of 700 and 750 ^oC

Loading method	CH_4 conversion (%)		CO_2 conversion (%)	
Reaction temperature (^oC)	700	750	700	750
Solvothermal (100% THF)	50	83	34	55
Hydrothermal method (15 h)	35	62	13	23

IV. CONCLUSION

The Ni/Al_2O_3 catalysts of various particle sizes were successfully prepared by using impregnation, solvothermal and hydrothermal methods. The metal particle sizes can be controlled in the length of 5 to 200 nm. The Ni/Al_2O_3 catalysts obtained from solvothermal and hydrothermal methods were applied for dry reforming reaction of CO_2 and CH_4. It was found that the Ni/Al_2O_3 catalysts of 5 nm particle size (obtained from solvothermal method) promoted approximately 20% higher CO_2 and CH_4 conversions than that of the 30 nm particle size (obtained from hydrothermal method). Moreover, the appropriate catalytic activation process should be investigated in detail in order to clarify the suitable hydrogen uptake, and the reduction temperature and period.

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