La promoted Ni/α-Al₂O₃ Catalysts for Syngas Methanation

Anmin Zhao, Weiyong Ying   , Haitao Zhang, Hongfang Ma, and Dingye Fang

Abstract—The Ni/α-Al₂O₃ catalysts with different amounts of La as promoter from 0 to 4 wt % were prepared, characterized and their catalytic activity was investigated in syngas methanation reaction. Effects of reaction temperature and lanthanum loading on carbon oxides conversion and methane selectivity were also studied. Adding certain amount of lanthanum to 10Ni /α-Al₂O₃ catalysts can decrease the average NiO crystallite diameter which leads to higher activity and stability while excessive addition would cause deactivation quickly. Stability on stream towards deactivation was observed up to 800 min at 500 °C, 0.1MPa and 600000 mL·g^{-1}·h^{-1}.

Keywords—Methanation; Nickel catalysts; Syngas methanation

I. INTRODUCTION

NATURAL gas is widely used as a low carbon, highly efficient and environment friendly fuel all over the world. It is well known that the reserves of oil and natural gas are limited to a range of 40-60 years. In the contrary, the reserves of coal will last for more than 150 years; and biomass is renewable energy source [1].The longer availability, the wish to improve the security of the energy supply and the possibility to reduce the green house gas emission by means of carbon capture and sequestration (CCS), are the main motivations to increase the use of these domestic resources. Large expected demand for gas, shortage of natural gas as well as high price of gas by other alternatives have made the manufacture of so-called substitute or synthetic natural gas (SNG) attractive [2]. Although various chemical processes for the production of SNG have been investigated, coal to SNG is known to be one of the major processes for producing SNG [3]-[4].

In the coal to SNG process, methane production through syngas methanation has been recognized as a key process [5]-[6]. Therefore, developing an efficient catalyst for the methanation reaction would be worthwhile. The requirements to be met by a suitable methanation catalyst are: (1) High activity at a low temperature of approximate 300 °C; (2) Sufficient stability at temperature of 500 °C or even higher. For reasons of activity, selectivity and price, nickel is the obvious choice for the active component. Considering that the catalyst will be exposed under high partial steam pressures at high temperatures, silica containing supports which would exhibit unstable performance cannot be used. Thus leaves alumina as the most logical choice of a support [2], [7]. Methane steam reforming on Ni/α-Al₂O₃ catalysts is the well-established commercial process for the production of hydrogen and synthesis gas [8]. Since syngas methanation reaction is the reverse reaction of methane steam reforming, we can initiate from this type of reforming catalyst.

It is known that nickel/alumina catalysts prepared by conventional impregnation method suffer from severe catalyst deactivation during the methanation reaction due to sintering. Rare earth elements which have been verified to have special electronic and structure effects on catalysts are investigated as promoters [9].In order to study the impact of La loading on catalyst activity and stability for syngas (carbon oxides and hydrogen) methanation, series 10Ni/α-Al₂O₃ catalysts were modified by different amounts of lanthanum and their properties were characterized by XRD, TPR, SEM, and TEM.

II. EXPERIMENTAL

A. Catalyst Preparation

Ni(NO₃)₂·6H₂O and La(NO₃)₃·nH₂O were supplied by Sinopharm Chemical Reagent Co., Ltd and used without further purification. Catalysts were prepared by impregnation of α-Al₂O₃ with the mixed solution of nickel and lanthanum nitrate at 80 °C for 12 h. After impregnation, the catalysts were dried at 120 °C for 12 h and calcined in static air at 550 °C for 6 h. The nickel loading was fixed at 10 wt % while La loading was varied from 0 to 4 wt%, resulting in catalytic systems called NA, 2La-NA, and 4La-NA, respectively. The letter 'N' and 'A' represent nickel and alumina, respectively. For comparison, nickel-free catalyst 2La/α-Al₂O₃ was prepared by the same method and called 2La-A.

B. Catalyst Characterization

Powder x-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2550 using Cu Kα radiation at 40 kV and 100 mA. XRD patterns were obtained over a 2θ range of 10-80°and a step size of 0.02°.Hydrogen temperature-programmed reduction (H₂-TPR) measurements were carried out on Micrometrics AutoChem Ⅱ 2920. Prior to the H₂-TPR measurements, 0.0200 g sample placed in a quartz U-tube reactor was pretreated in Ar stream at 500 °C for 1.0 h and then cooled to 50 °C. H₂-TPR was conducted with a gas mixture of 10 vol. % H₂ in Ar at a flow rate of 50 mL·min^{-1}. Temperature

A. M. Zhao is with Engineering Research Center of Large Scale Reactor Engineering and Technology, Ministry of Education, State Key Laboratory of Chemical Engineering,the East China University of Science and Technology, ShangHai, 200237 CN (e-mail: 062201@163.com).

W.Y. Ying is with Engineering Research Center of Large Scale Reactor Engineering and Technology, Ministry of Education, State Key Laboratory of Chemical Engineering, East China University of Science and Technology, ShangHai, 200237 CN (e-mail: wying@ecust.edu.cn).

H. T. Zhang is with Engineering Research Center of Large Scale Reactor Engineering and Technology, Ministry of Education, State Key Laboratory of Chemical Engineering, East China University of Science and Technology, ShangHai, 200237 CN (e-mail: zht@ecust.edu.cn).

H. F. Ma is with Engineering Research Center of Large Scale Reactor Engineering and Technology, Ministry of Education, State Key Laboratory of Chemical Engineering, East China University of Science and Technology, ShangHai, 200237 CN (e-mail: mark@ecust.edu.cn).

D. Y. Fang is with Engineering Research Center of Large Scale Reactor Engineering and Technology, Ministry of Education, State Key Laboratory of Chemical Engineering, East China University of Science and Technology, ShangHai, 200237 CN (e-mail: dyfang@ecust.edu.cn).

was raised to 800 °C with a heating rate of 10 °C·min^{-1}. Hydrogen consumption was measured by a thermal conductivity detector (TCD).

Scanning Electron Microscopy (SEM) was employed to obtain the surface morphology. SEM measurements were performed on an S-4800 electron microscope. Transmission electron microscope (TEM) images were taken by means of a JEM-1400 apparatus operating at 100KV. In order to obtain suitable samples, the catalyst powders were dispersed in ethanol by ultrasonic and than a drop of the solution was placed on a carbon-coated copper grid.

C. Syngas Methanation

Syngas (carbon oxides and hydrogen) methanation reactions were carried out in a 12 mm (inner diameter) fixed-bed reactor. The reactions were performed during 0.1-2.0 MPa, temperature range of 300-400 °C, while high temperature stability tests were carried out at 500 °C, 0.1MPa, and with 30 mol. % of water. Typically, 0.5000 g catalyst was used, and the total gas flow rate was 100mL·min-1, corresponding to a weight hourly space velocity (WHSV) of 12000 mL·g^{-1}·h^{-1}. The catalyst diluted with certain amount of inert Al_2O_3 was settled in the uniform temperature zone, where the axial temperature was measured with a thermocouple though the catalyst bed. Prior to the reaction, the catalyst was heated from ambient to 500 °C with a heating rate of 1 °C·min^{-1} and reduced for 2 h in situ by pure hydrogen. The catalyst was then cooled to 300 °C under nitrogen flow and the reaction started as gas flow was switched to the syngas (6.9 vol. % CO, 6.0 vol. % CO_2, 84.2 vol. % H_2, and 2.9 vol. % N_2). Flow rates of all gases were monitored by calibrated mass flow controllers (Brooks 5850 E).

Gas compositions of the inlet and outlet were analyzed by an on-line gas chromatography (Agilent 7890A series) equipped with one FID (flame ionization detector) and two TCD (thermal conductivity detector). Hydrocarbons from C_1 to C_6 were analyzed by a FID after separation with a HP-PLOT "S" Al_2O_3 column. N_2, CO and CO_2 were analyzed by a TCD after separation with two PropackQ and one 5Å molecular sieve columns (CO_2 did not enter this column). H_2 was analyzed using a TCD after separation with one PropackQ and one 5Å molecular sieve column. To calculate carbon oxides conversion, formation rate and selectivity of methane, the effluent gas were analyzed after steady-state operation under each condition.

III. RESULTS AND DISCUSSION

The catalysts as well as bare support were characterized by XRD and their patterns were shown in Fig. 1. It is noteworthy that all samples exhibited sharp diffraction peaks which indicate that all the catalysts were mainly present in the form of crystalline structure. The carrier was mainly composed of α-Al_2O_3, judging from the peaks on the XRD patterns (JCPDS card no.46-1212). Ni-loaded catalysts exhibit obvious reflection at 37.3°,43.2°,62.9° and 75.3° attributed to cubic NiO (JCPDS card no.73-1519). No lanthanum oxide crystalline phase was detected. These results suggested that lanthanum

species are finely dispersed on the catalysts surface and thereby result in the formation of small lanthanum particles that are below the detection limit of XRD measurements [12].
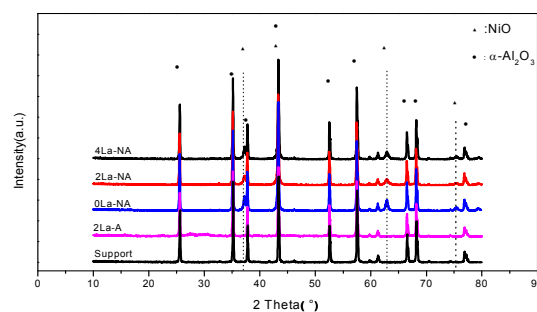

Fig. 1 XRD patterns of the catalysts

The crystallite sizes of NiO were calculated based on NiO (220) and NiO (311) plane reflection using the famous Scherrer equation. Average α-Al_2O_3 crystalline diameters were also calculated based on (104) and (116) plane and summaried in TableI. Average α-Al_2O_3 crystalline diameters were 45.5nm and 39.2nm for (104) and (116) plane, respectively. Thus, the α-Al_2O_3 crystalline was presented ellipsoid type and this can be confirmed by the SEM images in Fig.3 ((a) and (b)).

As listed in Table I, average NiO crystalline diameter decreasing as increasing lanthanum loading from 0 to 4 %. It reveals that adding lanthanum can increase nickel dispersion by decrease average NiO crystalline diameter from 18.0nm to 12.6nm. This dispersion effect can be seen clearly in TEM images in Fig. 3(c and d).

TABLE I
AVERAGE CRYSTALLINE DIAMETER CALCULATED FROM XRD PATTERNS

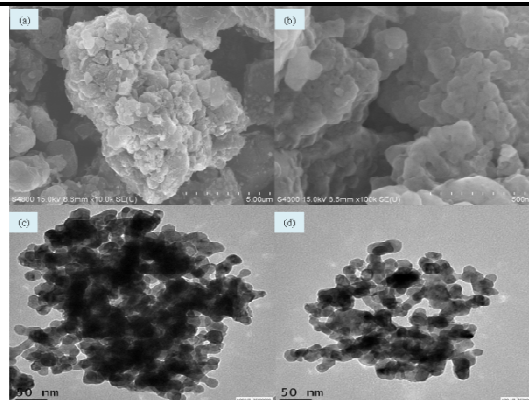| Catalyst	α-Al_2O_3(104) (nm)	α-Al_2O_3(116) (nm)	NiO(311) (nm)	NiO(220) (nm)
Support	45.3	39.5		
2La-A	46.0	39.7		
0La-NA	45.6	38.9	16.3	18.0
2La-NA	45.3	39.3	13.0	14.6
4La-NA	45.5	38.5	12.2	12.6

Fig. 2 SEM and TEM images. SEM micrographs of the support alumina (a) and (b), TEM images of 0La-NA (c) and 2La-NA (d)

TPR technique allows us not only to characterize the metal-support interactions but also to elucidate the role of additives as promoters in the reduction process [10]. Several TPR studies on nickel-supported catalysts have been undertaken [11]-[13], indicating that Ni^{2+} is directly reduced to metallic Ni^0 without any intermediate species, therefore each peak is believed to match a different species. Fig. 2 shows TPR results of the all samples, in which the overlapped peaks are deconvolved using Gaussian-type functions.
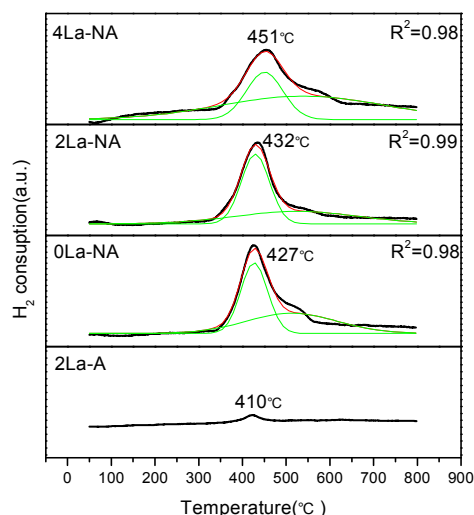

Fig. 3 TPR profiles of catalysts with La as promoter

After a mathematical treatment of the reduction profile, two elementary peaks that centered at 420-450 °C and 510-540 °C, respectively, could be well deconvolved (summarized in Table II). Low temperature peaks are generally attributed to the reduction of larger NiO particles which are similar in nature to pure bulk NiO, while the high temperature peaks are ascribed to the reduction of NiO which is in intimate contact with the oxide support [12]-[15]. The results revealed that addition of La can change the reduction characteristics of catalysts.

TABLE II
TPR DATA AFTER DECONVOLUTION USING GAUSSIAN-TYPE FUNCTIONS

Catalyst	T_m(°C)		Fraction of total area (%)	
	Low	High	Low	High
10Ni/α-Al₂O₃	427	513	51	49
10Ni-2La/α-Al₂O₃	430	530	57	43
10Ni-4La/α-Al₂O₃	451	539	31	69

Low temperature catalytic activity of the three nickel content catalysts, with lanthanum loading from 0 to 4 wt%, was studied at temperatures from 300 to 400 °C. Results under the condition of 12000h⁻¹ and 0.1MPa are summarized in Fig. 4(a), where conversions of carbon oxides are plotted as functions of reaction temperature. CO conversion increased with increasing temperature monotonely (except 4La-NA), and nearly 100% conversion of CO was achieved above 360 °C. CO_2 conversion

in this system also increases dramatically from negative values with temperature raised. This was probably owing to water gas shift reaction, which can produce CO_2 and cause the conversion of CO_2 keep minus apparently[16, 27]. As for 4La-NA, catalyst deactivation quickly (explain in detail later).
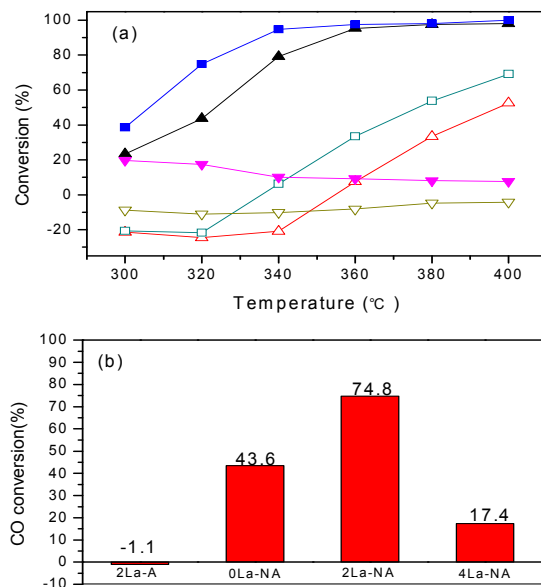

Fig. 4 Effect of temperature on carbon oxides conversion
(Solid symbols represent CO conversion and hollow symbols represent CO_2 conversion.) ▲: 0La-NA; ■□: 2La-NA; ▼ : 4La-NA

Effect of lanthanum loading on CO conversion under 320 °C, 0.1MPa and 12,000 mL·g⁻¹·h⁻¹ was plotted in Fig. 4(b). It should be noted that 2La/α-Al₂O₃ (2La-A) catalyst can be partially reduced to exhibit hydrogenation activity. Reverse water gas shift reaction which would produce CO can be catalyzed by 2La-A as is shown in Fig. 4(b). Thus, the conversion of CO exhibits -1.1% apparently. The conversion of CO increased rapidly from 43.6% to 74.8% with the increase of lanthanum from 0 to 2 wt%, and further addition of lanthanum results in a drastic decrease of CO conversion. The loss of activity with higher lanthanum content is due to the blockage of active sites by excess amounts of lanthanum introduced to the catalyst. Steady-state reaction experiments show that the addition of small amounts (2 wt %) of lanthanum improves the catalytic activity and stability significantly [16]. Some amount of lanthanum was effective for fine dispersion of nickel species during the reduction process through prevent nickel from being sintered, but addition of large amount of lanthanum was unfavorable for nickel dispersion due to the blocking of active sites [17]. When an excess amount of lanthanum was added, active nickel species (Ni^0) on the catalyst surface was reoxidized by the lattice oxygen of La_2O_3 [18]. Therefore, the optimal lanthanum loading is 2 wt% concluded from the above facts.

It should be noted that syngas methanation under present reaction conditions also leads to the production of higher hydrocarbons except for methane. Typical results obtained from 0La-NA and 2La-NA are shown in Fig. 5, where the influence of reaction temperature towards selectivity of hydrogenation products was presented. Selectivity of CH_4 (C_1) increases from 83 to 100% by increasing temperature from 300 to 360 °C. The main by-products formed below 360 °C are C_2-C_6 hydrocarbons. At temperatures above 360 °C, where conversion of CO is complete, formation of higher hydrocarbons is suppressed and the only hydrogenation product formed is methane. Therefore, the addition of lanthanum has limited effect on product distribution while temperature plays an important role.
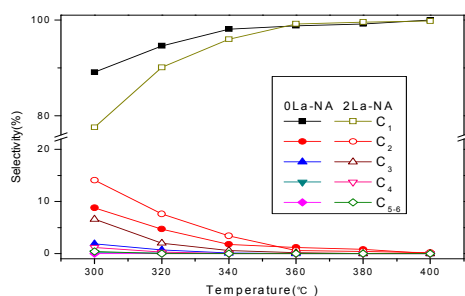

Fig. 5 Effect of temperature on product distribution over 0La-NA and 2La-NA

Requirement to be met by a suitable methanation catalyst is the sufficient stability under high temperature. The catalysts stability of 0La-NA and 2La-NA for syngas methanation were investigated on stream for 800min at 500 °C, 0.1MPa, 600000 $mL·g^{-1}·h^{-1}$, and with 30 mol. % stream. According to Fig. 6, catalyst 0La-NA deactivates quickly while 2La-NA possesses better high temperature stability. This can be explained by the important characteristics of 2La-NA including high oxygen storage capacity of the lanthanum oxide species and its ability to highly disperse nickel over the catalyst surface. Therefore, 2La-NA with the addition of La as promoter would be able to ensure long-term activity and stability compared with 0La-NA.
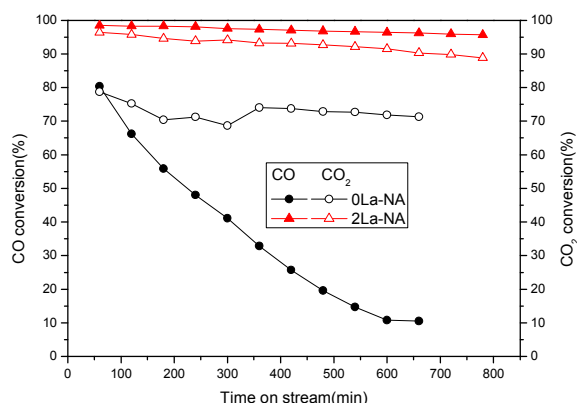

Fig. 6 High temperature stability test

IV. CONCLUSION

$10Ni/\alpha$-Al_2O_3 catalysts with La loadings ranging from 0 to 4% were prepared, and their properties were characterized. Several conclusions can be drawn from these investigations. First, the addition of lanthanum can change the reduction characteristics of catalysts. Second, doping certain amount of lanthanum can decrease the average NiO crystallite diameter which leads to higher activity and stability while excessive addition would cause deactivation quickly. Therefore, with 2 wt % La is optimal in this work. Third, adding La can change the product distribution slightly while temperature plays a more important role. Fourth, catalyst with 2 wt % La loading obtained better high temperature stability than La-free catalyst in our tests.

REFERENCES

[1] J. Kopyscinski, T. J. Schildhauer, and S. M. A. Biollaz, "Production of synthetic natural gas (SNG) from coal and dry biomass –A technology review from 1950 to 2009," *Fuel*, vol. 89, no. 8, pp. 1763–1783, August 2010.

[2] G. A. Mills, and F. W. Steffgen, "Catalytic Methanation," *Catal. Rev.*, vol. 8, no. 2, pp. 159–210, 1973.

[3] S. Hwang, J. Lee, U. G. Hong, J. G. Seo, J. C. Jung, D. J. Koh, H. Lim, C. Byun, and I. K. Song ."Methane production from carbon monoxide and hydrogen over nickel–alumina xerogel catalyst: Effect of nickel content," *J. Ind. Eng. Chem.*, vol. 17, pp. 154–157, July 2011.

[4] R. W. R. Zwart, and H. Boerrigter, "High Efficiency Co-production of Synthetic Natural Gas (SNG) and Fischer-Tropsch (FT) Transportation Fuels from Biomass," *Energy Fuels*, vol. 19, no. 2, pp. 591–597, Feb. 2005.

[5] P. Panagiotopoulou, D.I. Kondarides, and X.E.Verykios, "Selective methanation of CO over supported noble metal catalysts: Effects of the nature of the metallic phase on catalytic performance," *Appl.Catal.A:Gen.*,vol. 344, no. 1-2, pp. 45–54, July 2008.

[6] Z. Pan, M. Dong, X. Meng, X. Zhang, X. Mu, B. Zong, "Integration of magnetically stabilized bed and amorphous nickel alloy catalyst for CO methanation," *Chem. Eng. Sci.*, vol. 62, no. 10, pp. 2712–2717, May 2007.

[7] M. Kramera, K. Stowea, M. Duisberg, M. Reaser, S. Sticher, and W. F. Maier, "The impact of dopants on the activity and selectivity of a Ni-based methanation catalyst," *Appl.Catal.A:Gen.*,vol. 369, no. 1-2, pp. 42–52, November 2009.

[8] K. H. Hou, R. Hughes, "The kinetics of methane steam reforming over a Ni/α-Al₂O₃ catalyst," Chem. Eng. J., vol. 82, pp. 311–328, 2001.

[9] K.O. Xavier, R. Sreekala, K.K.A. Rashid, K. K. M. Yusuff, and B. Sen, "Doping effects of cerium oxide on Ni/Al2O3 catalysts for methanation," Catal. Today, vol. 49, no. 1-3, pp. 17–21, February 1999.

[10] J. Zhang, H. Y. Xu, X. L. Jin, Q. J. Ge, and W. Z. Li, "Characterizations and activities of the nano-sized Ni/Al₂O₃ and Ni/La-Al₂O₃ catalysts for NH₃ decomposition," *Appl.Catal.A:Gen.*,vol. 290, no. 1-2, pp. 87–96, August 2005.

[11] F.Ocampo, B. Louis, and A. C. Roger, "Methanation of carbon dioxide over nickel-based Ce0.72Zr0.28O2 mixed oxide catalysts prepared by sol-gel method," *Appl.Catal.A:Gen.*,vol. 369, no. 1-2, pp. 90–96, November 2009.

[12] C. W. Hu, J. Yao, H. Q. Yang, Y. Chen, and A. M. Tian, "On the Inhomogeneity of Low Nickel Loading Methanation Catalyst," *J. Catal.*, vol. 166, no. 1, pp. 1–7, February 1997.

[13] R. Molina, and G. Poncelet, "α-Alumina-Supported Nickel Catalysts Prepared from Nickel Acetylacetonate: A TPR Study," *J. Catal.*, vol. 173, no. 2, pp. 257–267, January 1998.

[14] A. M. Diskin, R. H. Cunningham, and R. M. Ormerod, "The oxidative chemistry of methane over supported nickel catalysts," *Catal. Today*, vol. 46, no. 2-3, pp. 147–154, November 1998.

[15] J. M. Rynkowski, T. Paryjczak, and M. Lenik, "On the nature of oxidic nickel phases in NiO/γ-Al2O3 catalysts," *Appl.Catal.A:Gen.*, vol. 106, no. 1, pp. 73–82, November 1993.

[16] S. Natesakhawat, O. Oktar, and U. S. Ozkan, "Effect of lanthanide promotion on catalytic performance of sol–gel Ni/Al$_2$O$_3$ catalysts in steam reforming of propane," *J. Molecular Catal. A: Chem.*, vol. 241, no. 1-2, pp. 133–146, November 2005.

[17] Y. Bang, J. G. Seo, and I. K. Song, "Hydrogen production by steam reforming of liquefied natural gas (LNG) over mesoporous Ni-La-Al$_2$O$_3$ aerogel catalysts: Effect of La content," Int. J. Hydrogen Energy, vol. 36, no. 14, pp. 8307–8315, July 2011.

[18] N. Laosiripojana, W. Sutthisripo, and S. Assabumrungrat, "Synthesis gas production from dry reforming of methane over CeO$_2$ doped Ni/Al$_2$O$_3$: Influence of the doping ceria on the resistance toward carbon formation," Chem. Eng. J., vol. 112, no. 1-3, pp. 13-22, September 2005.