Study on Ni/ZrO₂ catalyst preparation

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Abstract. In this work, the influence of catalyst preparation temperature on its structure was investigated. We have synthesized 12 different Ni/ZrO₂ catalysts by varying the calcination temperature, time, and active metal content, and these catalysts will be further used in the carbon dioxide methanation reaction. Structure and properties of the catalysts were determined using XRD and SEM analysis. Therefore, Ni content of the catalysts were measured by ICP-OES.
Regarding to the crystal size calculation using XRD data by Scherer equation, when calcination time was increased the average crystal size of nickel oxide was decreased from 42.38 nm to 38.93 nm whereas it decreased to 39.23 nm when the calcination temperature was increased. This shows that the distribution of active metals in the catalyst increases when the heat treatment parameters are increased. In addition, it can be assumed that the activity of the catalyst can be enhanced when the calcination temperature and time were increases.

Keywords: catalyst calcination time and temperature, x-ray diffraction, crystal size, impregnation.

1   Introduction

Coal makes 24 percent of resources consumed in world energy production and almost 40 percent of total electricity production is solely based on coal [1]. Even though world economy strongly depends on coal, its utilization is considered to be one of the main source of environmental pollution

Due to human activities such as industrialization and urbanization, the concentration of CO_2 released into the atmosphere has exceeded the limit that could cause the global warming, i.e. it has reached more than 440 ppm [2], [3]. Therefore, the carbon capture and storage (CCS) process has been developing rapidly in recent years to mitigate carbon dioxide emissions [3]–[7].

The main reaction used in the process is the CO_2 methanation reaction discovered by Sabatier, which is also being developed for use in combination with renewable energy

production [2]–[6], [8]–[10]. CO_2 methanation is a catalytic reaction. Noble metals such as Ru, Rh, Pd and Ni are the most suitable and widely studied for this reaction, and among them, Ni is drawing much attention due to its high activity, low cost and high abundance [4], [5], [7]–[13]. The only problem with Ni-based catalysts is deactivation due to carbon deposition. Therefore, in order to solve this problem and improve the activity and stability of Ni catalysts, researchers have studied various support materials such as Al_2O_3, SiO_2, CeO_2, ZrO_2, TiO_2 and hydrotalcite. Among these supports, ZrO_2 reduced the carbon deposition by hydrogen spillover phenomenon, and thus increased the activity and stability of the catalyst, so ZrO_2 support was widely studied [2], [4], [5], [9]–[11], [14].

Ni/ZrO_2 catalyst has a high degree of CO_2 conversion and nearly 100% selectivity to methane, thus a number of work has been done on this catalyst. For instance, adding promoters, varying precursor salts, comparing preparation methods and varying reaction parameters, etc. [2], [5], [6], [8], [11], [15]–[17].

The activity, structure, and properties of a catalyst depend greatly on the conditions under which it was synthesized, especially the calcination process. In order to synthesize a catalyst suitable for implementation to industrial scale, it is necessary to establish suitable parameters for its preparation. The calcination temperature of a catalyst is one of the main factors determining its activity, and the activity of supported metal catalysts strongly depends on the temperature and time of heat treatment [12], [18]. Therefore, in this work, we aimed to determine the effect of calcination temperature and time of Ni/ZrO_2 catalyst to its structure and properties.

2   Experimental

Following preparation parameters were varied in catalyst synthesis. Herein:
1. Nickel content: 5%, 20% and 50%
2. Calcination temperature: 400°C and 600°C
3. Calcination time: 4 and 6 hours

Metal concentration of the catalyst were analyzed by inductively coupled with plasma–optical emission spectrometer (ICP-OES, iCAP6500, Thermo Scientific). X-ray diffraction of the samples were performed by X-ray diffractometer (MAXima_X XRD-7000, Shimadzu Scientific Instruments) with Cu-Kα radiation (λ=1.541874 Å). The operating voltage and current were 40kV and 30mA, respectively. SEM images were taken by Scanning electron microscopy with energy dispersive spectroscopy TM-1000 at Field Research laboratory of Mongolian University of Science and Technology associated with Nagoya University of Japan.

2.1   Ni/ZrO2 catalyst preparation by impregnation method

Catalysts were developed by the well-known impregnation method [5], [6], [13], [19], [20]. Nickel nitrate (Ni(NO_3)$_2$·$6H_2O$, 99.9%, Tianjin Factory No.3 of Chemicals and reagents, China) and zirconium dioxide (ZrO_2, 99.9%, China) were used as received. Calculated amount of Ni(NO_3)$_2$·$6H_2O$ was dissolved in a small amount of

deionized water. After 30 minutes, measured amount of zirconium dioxide was added to the solution gradually with continuous stirring. The mixture were stirred in mortar and pestle until the solution containing active metal has completely deposited in the pores of support. Formerly the mixture was dried at 110°C for 12 hours and calcined at different temperatures and times. The lower and upper limits of calcination temperature and duration were chosen based on previous literature [2], [5], [7]–[9], [13], [14], [16] and heat treatment conditions were illustrated in Table 1.

Totally 12 different catalysts were prepared with nominal nickel contents of 5%, 20% and 50%, and at calcination temperatures of 400°C and 600°C for 4 and 6 hours.
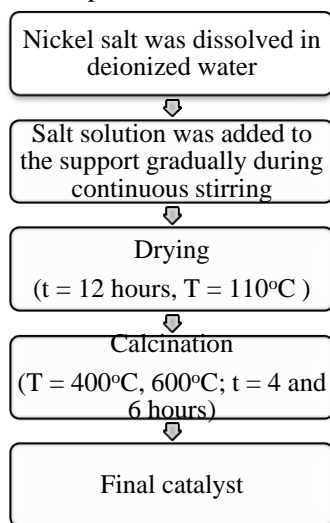
Nickel salt was dissolved in deionized water

⇩

Salt solution was added to the support gradually during continuous stirring

⇩

Drying
(t = 12 hours, T = 110°C)

⇩

Calcination
(T = 400°C, 600°C; t = 4 and 6 hours)

⇩

Final catalyst

Figure. 1. Impregnation method scheme of catalyst preparation.

Name of the catalysts corresponding to the preparation conditions are shown below.

Table 1. Catalyst name and corresponding preparation parameter

No.	Name	Metal content, %	Calcination temperature, °C	Calcinaton time, hr
1	Cat – 1	5	400	4
2	Cat – 2	20	400	4
3	Cat – 3	5	400	6
4	Cat – 4	20	400	6
5	Cat – 5	5	600	4
6	Cat – 6	20	600	4
7	Cat – 7	5	600	6
8	Cat – 8	20	600	6
9	Cat – 9	50	400	4
10	Cat – 10	50	400	6
11	Cat – 11	50	600	4
12	Cat – 12	50	600	6

3   Results and discussion

Ni/ZrO$_2$ catalysts were synthesized by impregnation method at different preparation conditions mentioned above. Synthesized catalysts were in a form of grey powder and the color was changed from light to dark grey as the nickel content increases.

3.1   XRD result of Ni/ZrO$_2$ catalyst

Phase identification analysis were carried for the catalysts using XRD-7000 X-ray diffractometer at Instrumental Analysis Center of Institute of Physics and Technology in Mongolian Academy of Science.

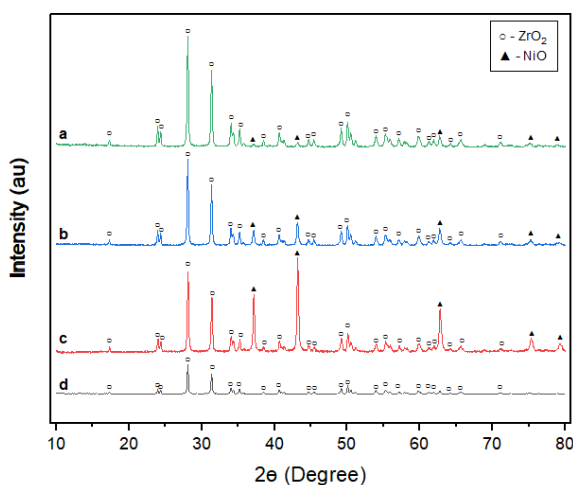### 3.1.1. X-ray diffractogram of Ni/ZrO$_2$ catalysts with different Ni contents

Figure. 2. XRD patterns of catalysts: a. 5% Ni/ZrO$_2$ (Cat-1), b. 20% Ni/ZrO$_2$ (Cat-2), c. 50% Ni/ZrO$_2$ (Cat-9), d. Support (ZrO$_2$).

XRD patterns of 5% Ni/ZrO$_2$, 20% Ni/ZrO$_2$ and 50% Ni/ZrO$_2$ catalysts were shown in Fig. 2. The reflections at 2θ = 37.26°, 43.34°, 62.83°, 75.45° and 79° are assigned to NiO phase while the signals at   2θ = 17.44°, 24.06°, 24.47°, 28.20°, 31.47°, 34.13°, 34.44°, 38.63°, 40.75°, 44.79°, 49.27°, 50.18°, 50.58°, 54.06°, 55.35°, 57.26°, 59.89°, 61.87°, 65.68°, 71.17°, 72.46° and 78.98° are ascribed to ZrO$_2$. The diffraction peaks were in agreement with the previous literature's results [2], [4], [16], [21], [5]–[9], [11], [13], [15].

It can be seen that peak intensity corresponding to NiO phase increased with the Ni content.

3.1.2. X-ray diffractogram of Ni/ZrO$_2$ catalysts processed at different calcination temperatures
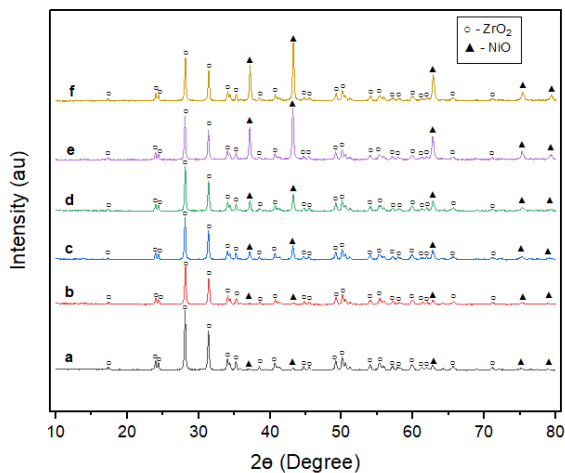

Figure. 3. XRD patterns of catalysts: a. 5% Ni/ZrO$_2$ /400ºC/ (Cat-3), b. 5% Ni/ZrO$_2$ /600ºC/ (Cat-4), c. 20% Ni/ZrO$_2$ /400ºC/ (Cat-7), d. 20% Ni/ZrO$_2$ /600ºC/ (Cat-8), e. 50% Ni/ZrO$_2$ /400ºC/ (Cat-10), f. 50% Ni/ZrO$_2$ /600ºC/ (Cat-12).

XRD patterns for 5%Ni/ZrO$_2$ catalysts calcined at 400ºC and 600ºC temperatures for 6 hours were shown in (a) and (b), for 20%Ni/ZrO$_2$ catalysts calcined at 400ºC and 600ºC temperatures for 6 hours were shown in (c) and (d), and for 50%Ni/ZrO$_2$ catalysts calcined at 400ºC and 600ºC temperatures for 6 hours were shown in (e) and (f) of Fig.3, respectively.

From the diffractogram, it can be seen that the diffractogram peaks became sharper when the calcination temperature increases. It might indicate that the crystallinity of the phases were enhanced when increasing the parameter.

3.1.3. X-ray diffractogram of Ni/ZrO$_2$ catalysts processed for different calcination time

XRD patterns of 5%Ni/ZrO$_2$ catalysts calcined at 600ºC for 4 and 6 hours were shown in (a) and (b), for 20%Ni/ZrO$_2$ catalysts calcined at 600ºC for 4 and 6 hours were shown in (c) and (d), and for 50%Ni/ZrO$_2$ catalysts calcined at 600ºC for 4 and 6 hours were shown in (e) and (f) of Fig.4, respectively.

It can be seen that, the diffractogram peaks were also sharpened when increasing the calcination time which also may indicate that the phase crystallinity was increased when increasing the duration of heat treatment.
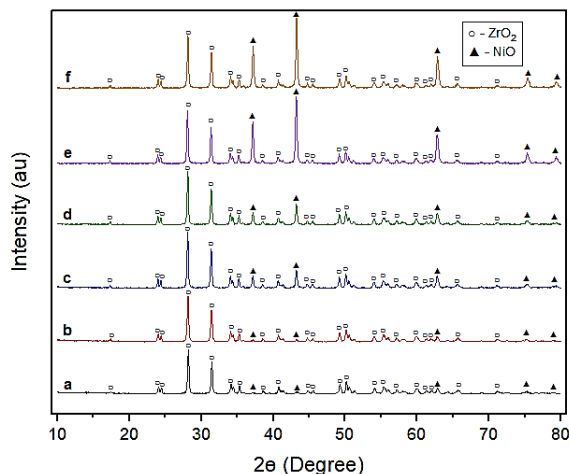
Figure. 4. XRD patterns of catalysts: a. 5% Ni/ZrO$_2$ /4 hours/ (Cat-5), b. 5% Ni/ZrO$_2$ /6 hours/ (Cat-6), c. 20% Ni/ZrO$_2$ /4 hours/ (Cat-7), d. 20% Ni/ZrO$_2$ /6 hours/(Cat-8), e. 50% Ni/ZrO$_2$ /4 hours/ (Cat-11), f. 50% Ni/ZrO$_2$ /6 hours/ (Cat-12).

Crystal sizes of NiO and ZrO$_2$ phases were calculated using FWHM values from XRD result by Scherer equation and it's shown in Table 2.

Table 2. Average crystal size of phases

No.	Sample name	Crystal size, nm	
		NiO	**ZrO$_2$**
1	Support	-	40.50
2	Cat – 1	42.38	43.73
3	Cat – 2	42.08	34.53
4	Cat – 3	38.93	26.83
5	Cat – 4	41.08	30.88
6	Cat – 5	39.23	29.31
7	Cat – 6	34.96	33.26
8	Cat – 7	35.88	28.21
9	Cat – 8	39.26	31.67
10	Cat – 9	38.21	32.62
11	Cat – 10	42.28	35.17
12	Cat – 11	44.76	33.80
13	Cat – 12	37.13	34.34

According to the table, the crystal size of NiO and ZrO$_2$ phases were decreased when calcination temperature and time are increased. For instance, the crystal size of NiO of Cat-1 (5% Ni, calcined at 400ºC for 4 hours) was 42.38 nm whereas the crystal size of Cat-3 (5% Ni, calcined at 400ºC for 6 hours) were 38.93 nm. Similarly, the crystal size was decreased when increasing the calcination temperature to 600ºC (Cat-5) to 39.23 nm. Same trend was observed for catalysts with 20% of nickel content and interestingly

the opposite trend was observed for catalysts with 50% nickel content. This corresponds to the fact that, as mentioned in the literature [4], high metal loading reduces its dispersion when preparing catalysts by impregnation method.

It was reported that in few studies, the calcination temperature had shown significant impact on the crystallite sizes of the active metal as well as its dispersion and therefore it has positively affected on the catalyst activity and stability [12], [18]. Moreover, it has been noted that the activity of the catalyst depends on particle size of the nickel oxide [15]. Summing up from this, it can be considered that the distribution of metals in our synthesized catalyst were increased when the calcination temperature and time were increased. In addition, further research will be held to determine the effect of the change in crystal size to the catalyst activity.
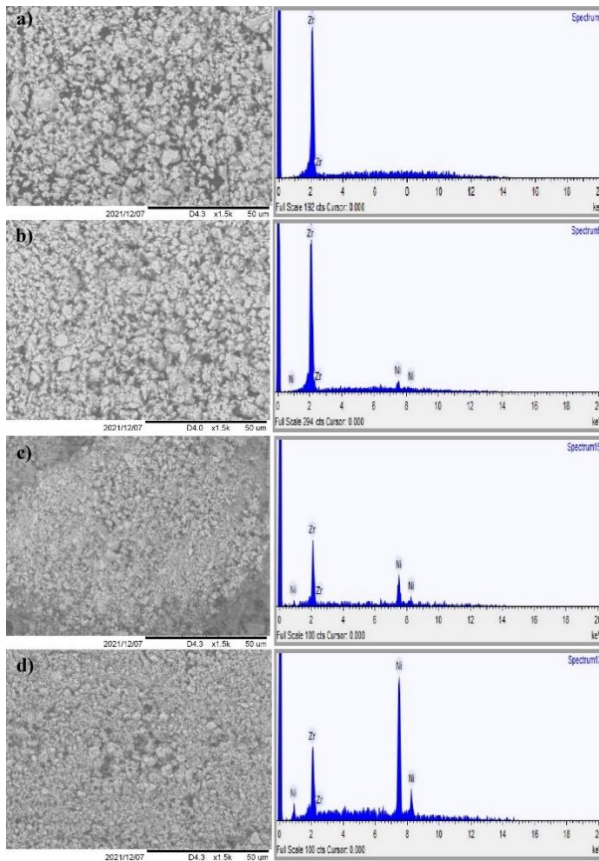
3.2   SEM analysis result of Ni/ZrO₂ catalyst

Figure. 5. SEM image and EDSpectra: a. Support b. Ni/ZrO₂, c. 20% Ni/ZrO₂ d. 50% Ni/ZrO₂.

SEM-EDS analysis were conducted for synthesized catalysts at Field research center of Mongolian University of Science and Technology in association with Nagoya University. Analysis results are illustrated in following figures.

Regarding to the figure, no other elements were observed other than nickel and zirconium, which means that the final catalysts doesn't have any impurities. Therefore, as the nickel content increases the corresponding peak intensity were shown to be increased.

Elemental composition of catalysts determined by SEM-EDS was shown in the following table.

Table 3. Elemental composition

Element	Content, %			
	Support	**Cat – 7**	**Cat – 8**	**Cat – 12**
Ni	-	14.8	58.9	87.0
Zr	100.0	85.2	41.1	13.0

In the figure below, SEM images and SEM-EDS spectra of catalysts with same nickel content and prepared at 400ºC for 4 hours and 600ºC for 6 hours, were compared.
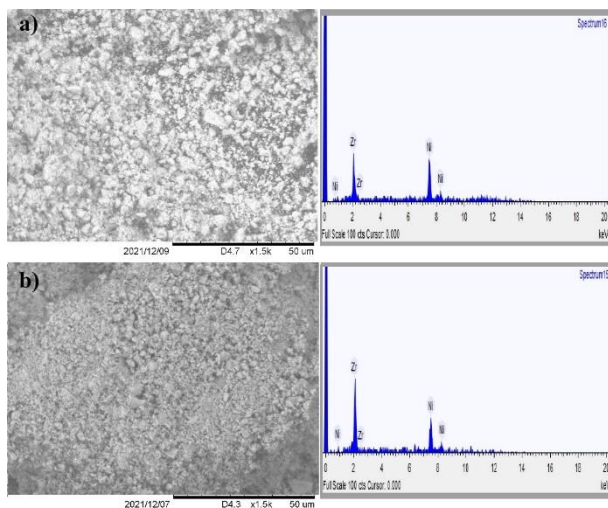

Figure. 6. SEM image and EDSpectra: a. 20% Ni/ZrO$_2$ (400ºC, 4 hours) b. 20% Ni/ZrO$_2$ (600ºC, 6 hours).

According to the image, the catalyst prepared under high temperature for long period of time has more homogenous structure and smaller particles than the catalyst prepared at lower temperature for a short period of time. Therefore, it's in agreement with the XRD result and crystal size calculation.

3.3   ICP-OES analysis result of Ni/ZrO$_2$ catalyst

The nominal nickel contents of catalysts were estimated to be 5%, 20% and 50%, and its content were determined using ICAP-6500 ICP-OES at Central Geological Laboratory.

Table 4. Nickel content of catalysts

No.	Sample name	Ni content, %	
		Nominal value	Experimental value
1	Cat – 1	5	3.86
2	Cat – 7	5	3.90
3	Cat – 8	20	17.81
4	Cat – 12	50	41.76

The experimental value of nickel content usually tends to be less than the nominal value [6]. According to the result of ICP-OES measurement in Table 4, the experimental value of nickel content was less than the calculated value for this work. However, the difference between experimental and nominal value was not that big meaning that the active metal has deposited on the support successfully.

4   Conclusion

According to the results of XRD, SEM and ICP-OES analysis, the catalysts we intend to obtain were formed free of any impurities and have metal content close to the nominal value.

From the X-ray diffractogram and crystal size calculation results of the catalysts, increasing the calcination temperature and time have led to a rise in crystallinity of the phases and a decrease in the crystal size. This indicates an increase in active metal dispersion, and it has been mentioned in previous works that increased dispersion has a positive effect on catalyst activity. Therefore, in our next research work, we will continue this work and investigate the effect of calcination temperature, time, and further crystallite size on the catalytic activity.

Acknowledgments

References

1. Narangerel. J, Basics of Coal Chemical Technology. 2011.
2. J. Martínez et al., High selectivity and stability of nickel catalysts for CO2 Methanation: Support effects, Catalysts, 9-1 (2019). https://doi.org/10.3390/catal9010024

3. K. O. Yoro and M. O. Daramola, CO2 emission sources, greenhouse gases, and the global warming effect, no. August. Elsevier Inc., 2020. https://doi.org/10.1016/B978-0-12-819657-1.00001-3

4. L. Hu and A. Urakawa, Continuous CO2 capture and reduction in one process: CO2 methanation over unpromoted and promoted Ni/ZrO2, J. CO2 Util., 25 (2018), pp. 323–329. https://doi.org/10.1016/j.jcou.2018.03.013

5. L. Li, Y. Wang, Q. Zhao, and C. Hu, The effect of si on co2 methanation over ni-xsi/zro2 catalysts at low temperature, Catalysts, 11-1 (2021), pp. 1–14. https://doi.org/10.3390/catal11010067

6. F. Ocampo, B. Louis, A. Kiennemann, and A. C. Roger, CO2 methanation over Ni-Ceria-Zirconia catalysts: Effect of preparation and operating conditions, IOP Conf. Ser. Mater. Sci. Eng., 19-1 (2011). https://doi.org/10.1088/1757-899X/19/1/012007

7. G. Zafeiropoulos et al., Developing nickel–zirconia Co-precipitated catalysts for production of green diesel, Catalysts, 9-3 (2019). https://doi.org/10.3390/catal9030210

8. M. Vissanu, P. Nopadol, P. Nat, G. Xineng, L. Chunshan, and R. Thirasak, Low Temperature Methanation of CO2 on High Ni Content Ni-Ce-ZrO2 Catalysts Prepared via One-pot Hydrothermal Synthesis, Catalysts, 10-1 (2020), pp. 1–10. https://doi.org/10.3390/catal10010032

9. L. Atzori, E. Rombi, D. Meloni, M. F. Sini, R. Monaci, and M. G. Cutrufello, CO and CO2-Methanation on Ni/CeO-ZrO2 Soft-Templated Catalysts, Catalysts, 9 (2019), pp. 2–15. https://doi.org/10.3390/catal9050415

10. P. Frontera, A. Macario, M. Ferraro, and P. L. Antonucci, Supported catalysts for CO2 methanation: A review, Catalysts, 7-2 (2017), pp. 1–28. https://doi.org/10.3390/catal7020059

11. M. S. Lanre et al., Catalytic performance of lanthanum promoted Ni/ZrO2 for carbon dioxide reforming of methane, Processes, 8-11 (2020), pp. 1–15. https://doi.org/10.3390/pr8111502

12. H. Wu et al., Effects of calcination temperatures on the structure-activity relationship of Ni-La/Al2O3 catalysts for syngas methanation, RSC Adv., 10-7 (2020), pp. 3166–3174. https://doi.org/10.1039/C9RA09674D

13. L. Zhao et al., Synergistic effect of oxygen vacancies and ni species on tuning selectivity of ni/zro 2 catalyst for hydrogenation of maleic anhydride into succinic anhydride and γ-butyrolacetone, Nanomaterials, 9-3 (2019). https://doi.org/10.3390/nano9030406

14. D. C. D. Da Silva, S. Letichevsky, L. E. P. Borges, and L. G. Appel, The Ni/ZrO 2 catalyst and the methanation of CO and CO 2, Int. J. Hydrogen Energy, 37-11 (2012), pp. 8923–8928. https://doi.org/10.1016/j.ijhydene.2012.03.020

15. S. Galanov, O. Sidorova, and O. Magaev, Dependence of the preparation method on the phase composition and particle size of the binary NiO-ZrO2 system oxides, IOP Conf. Ser. Mater. Sci. Eng., 597-1 (2019), pp. 1–6. https://doi.org/10.1088/1757-899X/597/1/012018

16. B. Buyan-Ulzii, O. Daariimaa, C. Munkhdelger, G. Oyunbileg, and B. Enkhsaruul, Effect of nickel precursor and catalyst activation temperature on methanation performance, Mong. J. Chem., 19-45 (2018), pp. 12–18. https://doi.org/10.5564/mjc.v19i45.1084

17. K. Stangeland, D. Kalai, H. Li, and Z. Yu, CO2 Methanation: The Effect of Catalysts and Reaction Conditions, Energy Procedia, 105-1876 (2017), pp. 2022–2027. https://doi.org/10.1016/j.egypro.2017.03.577

18. A. S. Al-Fatesh et al., Effect of pre-treatment and calcination temperature on Al2O3-ZrO2 supported Ni-Co catalysts for dry reforming of methane, Int. J. Hydrogen Energy, 44-39 (2019), pp. 21546–21558. https://doi.org/10.1016/j.ijhydene.2019.06.085

19. N. M. Deraz, The comparative jurisprudence of catalysts preparation methods: I. precipitation and impregnation methods, J. Ind. Environ. Chem., 2-1 (2018), pp. 19–21.

20. J. A. Schwarz, C. Contescu, and A. Contescu, Methods for Preparation of Catalytic Materials, Chem. Rev., 95-3 (1995), pp. 477–510. https://doi.org/10.1021/cr00035a002
21. G. Rajesh, S. Akilandeswari, D. Govindarajan, and K. Thirumalai, Facile precipitation synthesis, structural, morphological, photoluminescence and photocatalytic properties of Ni doped ZrO2 nanoparticles, Mater. Res. Express, 6-10 (2019). https://doi.org/10.1088/2053-1591/ab405e