Available online at BCREC website: https://bcrec.id

Bulletin of Chemical Reaction Engineering & Catalysis, 17 (2) 2022, 278-285

Research Article

Synthesis and Characterization of Mesoporous Carbon Supported Ni-Ga Catalyst for Low-Pressure CO_2 Hydrogenation

Uwin Sofyani, Yuni K. Krisnandi, Iman Abdullah*

Solid Inorganic Framework Laboratory, Department of Chemistry, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Depok-16424, Indonesia.

Received: 7th January 2022; Revised: 22nd February 2022; Accepted: 23rd February 2022
Available online: 2nd March 2022; Published regularly: June 2022

Abstract

In this study, the atmospheric-pressure hydrogenation of CO_2 was carried over bimetallic Ni-Ga catalyst supported on mesoporous carbon (MC). MC was successfully prepared using the soft-template method as proven by Fourier Transform Infra Red (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscopy - Energy Dispersive X-Ray Spectroscopy (SEM-EDS), Brunauer–Emmett–Teller Surface Area Analyzer (BET SAA), and Transmission Electron Microscopy (TEM) characterizations. The Ni-Ga/MC catalyst was synthesized using the impregnation method, and based on the XRD characterization, the formation of bimetallic Ni-Ga on the MC support is confirmed. The EDS mapping image shows the uniform distribution of the bimetallic Ni-Ga on the MC surface, especially for the Ni_5Ga_3/MC and $NiGa_3$/MC catalysts. Moreover, the TEM images show an excellent pore size distribution. The formation of Ni-Ga alloy was identified as an active site in the CO_2 hydrogenation. Ni_5Ga_3/MC catalyst exhibited a 10.80% conversion of CO_2 with 588 µmol/g formaldehyde at 1 atm, 200 °C, and H_2/CO_2 ratio of 3/1.

Copyright © 2022 by Authors, Published by BCREC Group. This is an open access article under the CC BY-SA License (https://creativecommons.org/licenses/by-sa/4.0).

Keywords: CO_2 Hydrogenation; Bimetallic catalyst; Ni-Ga; Mesoporous Carbon

How to Cite: U. Sofyani, Y.K. Krisnandi, I. Abdullah (2022). Synthesis and Characterization of Mesoporous Carbon Supported Ni-Ga Catalyst for Low-Pressure CO_2 Hydrogenation. *Bulletin of Chemical Reaction Engineering & Catalysis*, 17(2), 278-285 (doi: 10.9767/bcrec.17.2.13377.278-285)

Permalink/DOI: https://doi.org/10.9767/bcrec.17.2.13377.278-285

1. Introduction

CO_2 is a greenhouse gas that is responsible for global warming. On the other hand, CO_2 hydrogenation is the reaction that can produce methanol, dimethyl ether (DME), formic acid, and also formaldehyde [1,2]. Therefore, CO_2 hydrogenation is beneficial in mitigating global warming and provides value-added chemical products. Unfortunately, the very stable and inert nature of CO_2 makes it difficult to react, so CO_2 activation requires a high-energy substance at high pressure. In addition, direct hydrogenation will produce water product and an undesired reverse water gas shift (rWGS) reaction. The formation of excess water can interfere with the product hydrogenation and indicate the decrease of catalyst performance. Therefore, an active and selective catalyst is highly needed for an effective and efficient reaction.

A new type of catalyst, a mixture of two metals or bimetal, was reported to have good activity and selectivity for CO_2 hydrogenation at atmospheric pressure [3]. Studt *et al.* [4], in 2014, firstly reported that the Ga_3Ni_5 catalyst has

---

* Corresponding Author.
Email: iman.abdullah@sci.ui.ac.id (I. Abdullah);
Telp: +62-856-7735857

good activity, selectivity, and stability for the CO_2 conversion with 100% selectivity of methanol and DME at atmospheric pressure. Good selectivity of Ni_5Ga_3 catalyst for methanol production is also reported [5–7]. The catalytic activity of a catalyst can be increased by supporting the catalyst. Many previous studies have reported silica and alumina as support materials in the CO_2 hydrogenation to methanol [8]. No studies have reported the application of mesoporous carbon (MC) as Ni-Ga support. MC has characteristics that greatly assist its function as a catalyst support material. These characteristics are high chemical, mechanical, thermal stability, and also it is widely available in nature. In addition, MC has a controlled and stable pore structure that makes it possible to disperse the active phase [9]. The application of MC as catalyst support has been widely reported [10–12]. Recently, our research group has reported the good performance of the Ni-phenanthroline complex supported on MC as a catalyst in the CO_2 carboxylation with phenylacetylene under atmospheric pressure [13].

In this work, we investigate the atmospheric-pressure hydrogenation of CO_2 using the Ni-Ga catalyst supported by MC. The support and the series of catalysts were synthesized using a soft-template and impregnation method, respectively. The catalytic performance Ni-Ga/MC catalyst was also compared with Ni/MC and Ga/MC. The hydrogenation reaction was carried out in a fixed-bed tubular reactor at low-atmospheric pressure with H_2 to CO_2 molar ratio of 3:1 by varying reaction temperature at 150 °C, 170 °C, 200 °C, and 250 °C. The low-pressure condition was chosen because it has several advantages over the reaction at high pressure, such as a simpler process, lower cost and more applicable to small scale equipment [4]. In addition, by selecting the hydrogenation reaction conditions at lower pressures, it is also possible to shift the hydrogenation products towards the formation of products with lower reduction states, such as formaldehyde. This is interesting to investigate, considering the many uses of formaldehyde as a precursor in various chemical industries, as well as to provide an alternative pathway for formaldehyde synthesis.

2. Materials and Methods

2.1 Materials

Phloroglucinol, Pluronic F-127, gallium (III) nitrate were provided by Sigma Aldrich. Nickel (II) nitrate and ethanol (99 %v/v) were obtained from Merck (Germany). Hydrochloric acid (HCl) (37 %v/v) and formaldehyde (37 %v/v) were acquired from PT. Smart Lab Indonesia (Jakarta), distilled water was purchased from CV Satya Darmawan. High purity gases: hydrogen, nitrogen, carbon dioxide, and argon were procured from CV Retno Gas.

2.2 Methods

2.2.1 MC support synthesis

The soft-template method synthesized MC support, adopted from previously reported studies [12,14]. Briefly, phloroglucinol and pluronic F-127 were solvated in the mixture of water and ethanol 9:10 (w/w) at room temperature. After the copolymer was utterly dissolved, 37% (w/w) HCl was appended to the mixture, then 30 minutes stirred. Under continuously stirring, the mixture was added by 37% (w/w) formaldehyde. After 1-2 hours, the two layers will form, and then the base layer was taken and stirred for 12 hours. The decantation monolith was then cured in an autoclave for 24 hours at 100 °C. The next step is carbonizing the material in a tubular furnace under N_2 flow with the following conditions: a temperature of 100-400 °C, 400-850 °C, and 850 °C with the heating rate of 1 °C/min, 5 °C/min, and kept at 2 hours, respectively. Under N_2 flow, carbonized MC cooled down to room temperature.

2.2.2 Catalyst preparation

The series of Ni-Ga/MC catalysts were prepared using the incipient wetness impregnation method. A mixed Ni nitrate and Ga nitrate solution were sprayed onto the MC to form a paste. The paste was dried at room temperature, then an aqueous solution of Ni-Ga nitrate was resprayed. This step is repeated until the aqueous solution of Ni-Ga nitrate is used up. Next, the sample catalyst was aged for 24 hours. After that, the catalyst sample was reduced under H_2 flow at 700 °C for 2 h. Aqueous solutions of Ni nitrate and Ga nitrate were varied at the molar ratios of Ni/Ga (1/3, 3/3, and 5/3) with a total metal loading of 30% of the MC. For comparison, Ni/MC and Ga/MC were also prepared by the same procedure. The pre-

Table 1. Prepared catalysts

No	Molar Ratio Ni/Ga	Catalysts
1	5/3	Ni_5Ga_3/MC
2	3/3	NiGa/MC
3	1/3	$NiGa_3$/MC
4	-	Ni/MC
5	-	Ga/MC

pared catalyst abbreviations are presented in Table 1.

2.2.3 Catalyst characterizations

Functional groups and absorption spectra of material were characterized by Alpha Bruker FTIR spectrometer using KBr pellet. The XRD pattern measurement was performed with an XRD PANalytical: X'Pert Pro XRD 2318 under Cu-Kα 1.54 Å radiation. The instrument was operated at 30 mA and 40 kV with a time per-step 0.02. The surface area of support and catalysts was analyzed on a Surface Area Analyzer (SAA) Quantachrom QuadraWin ©2000-16 Surface Area and Pore Analyzer at 77.3 K. SEM-EDS mapping was investigated using SEM-EDS Hitachi SU-3500. TEM images were collected using the FEI Tecnai D2360 SuperTwin electron microscope operating at 200 kV acceleration voltage.

2.2.4 Catalytic activity test

The catalytic activity was analyzed at atmospheric pressure in a tubular fixed-bed reactor. The catalyst bed volume was 1.17 cm^3. The resulting products were analyzed using gas chromatography (GC) equipped with Porapak-Q and RTX-1 column connected to a thermal conductivity detector (TCD) and Flame Ionization Detector (FID), respectively. CO_2 conversion was investigated using GC Shimadzu TCD-8A. Meanwhile, the product hydrogenation was analyzed using GC Shimadzu FID 2014. The injector, column, and detector temperature of TCD were set up at 100 °C, 60 °C, and 100 °C, respectively. As for FID is 200 °C, 150 °C, and 200 °C, respectively. The carrier gas for the injected sample inside the GC TCD and FID was argon and nitrogen, respectively.

3. Results and Discussion

3.1 Catalyst Characterizations

Functional groups and absorption spectra of MC and MC supported Ni-Ga catalyst were investigated by FTIR, as shown in Figure 1. The resulting characterization of MC before carbonization (MC-BC) shows several peaks at 3400 cm^{-1}, 2900 cm^{-1}, 1625 cm^{-1}, 1462 cm^{-1}, and 1100 cm^{-1} that indicate the functional group of O−H stretch, C−H stretch, O−H bending, C−H bending, and C−O bending, respectively. These peaks are attributed to the remaining F-127 template and phloroglucinol precursor. However, the disappearing peaks in the MC spectrum after carbonization (MC-AC) indicate that the carbonization has been conducted successfully. The same spectrum of MC-AC was also seen in Ni/MC, Ga/MC, $NiGa_3$/MC, NiGa/MC, and Ni_5Ga_3/MC, indicating that metal impregnation did not affect the MC support. However, this needs to be further confirmed with other characterizations.

XRD patterns of MC support and MC supported Ni-Ga catalyst are pointed in Figure 2. Two peaks of MC at 2θ = 24.05° (002) and 43.56° (100) reveal the presence of graphite

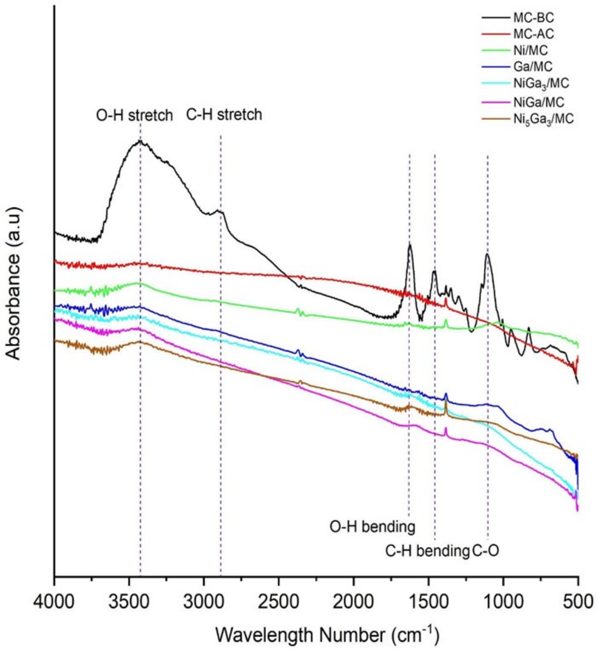


Figure 1. FTIR Spectra of MC and Ni-Ga/MC.

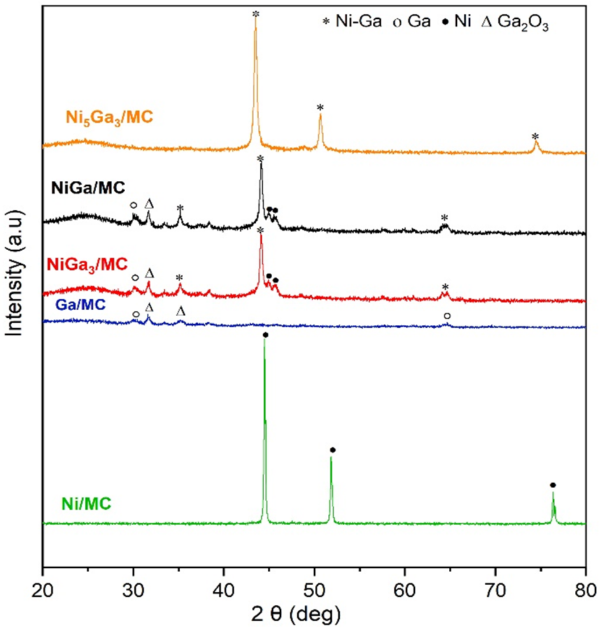


Figure 2. X-Ray diffractogram of MC and Ni-Ga/MC.

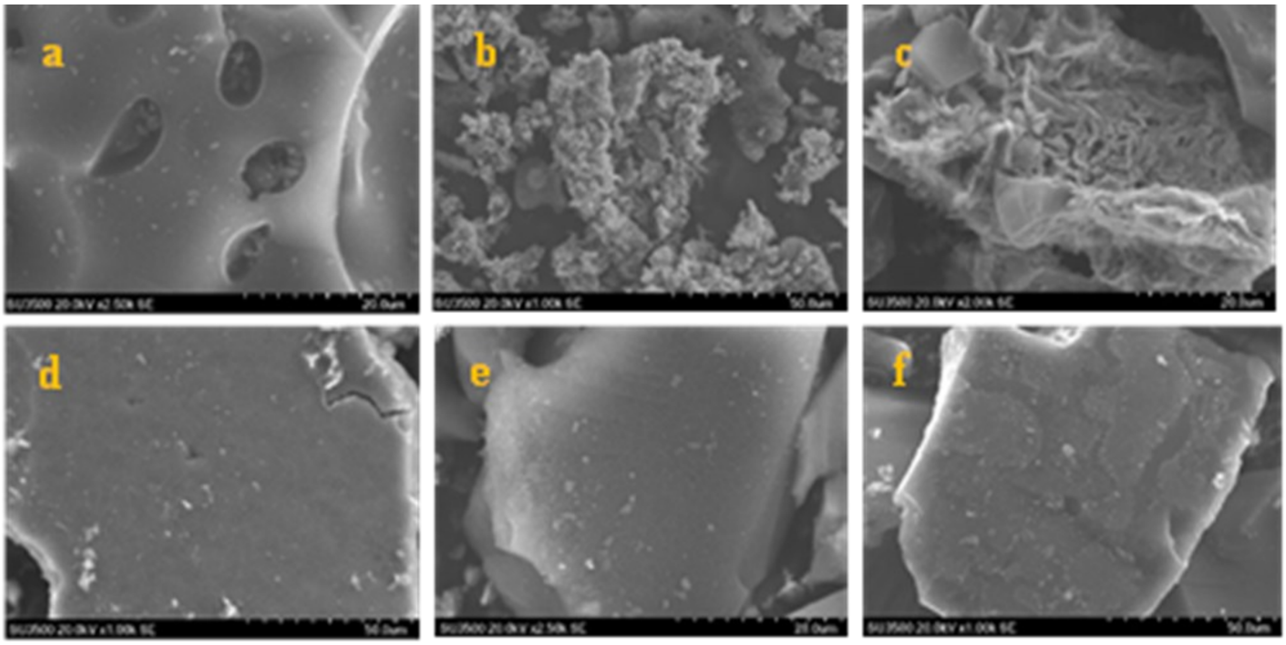
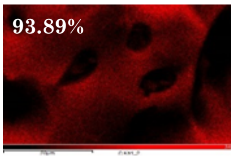
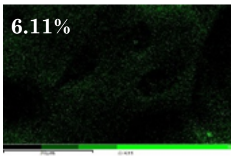
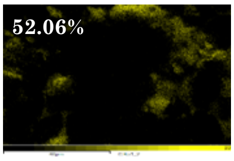
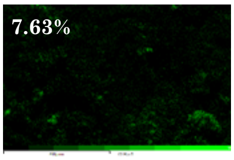
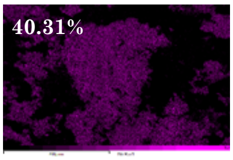
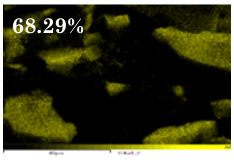
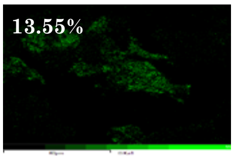
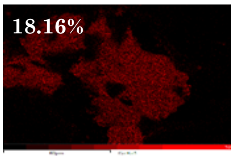
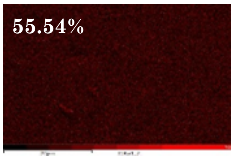
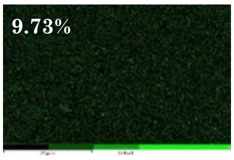
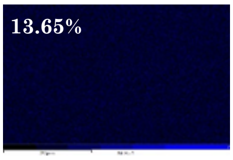
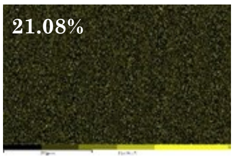
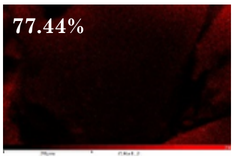
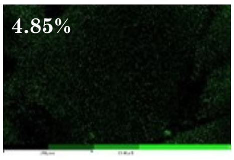
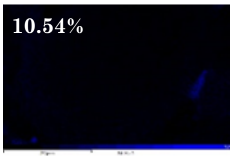
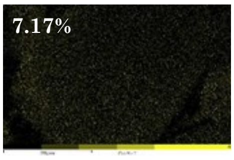
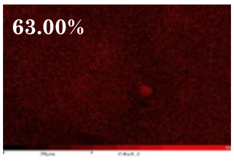
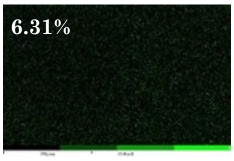
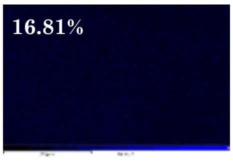
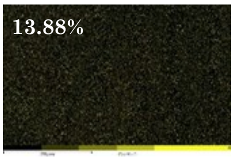


Figure 3. SEM figure of (a) MC, (b) Ni/MC, (c) Ga/MC, (d) $NiGa_3$/MC, (e) NiGa/MC, and (f) Ni_5Ga_3/MC.

Table 2. EDS mapping and elemental composition of prepared material.

Material	Element			
	C	O	Ni	Ga
MC	 93.89%	 6.11%		
Ni/MC	 52.06%	 7.63%	 40.31%	
Ga/MC	 68.29%	 13.55%		 18.16%
$NiGa_3$/MC	 55.54%	 9.73%	 13.65%	 21.08%
NiGa/MC	 77.44%	 4.85%	 10.54%	 7.17%
Ni_5Ga_3/MC	 63.00%	 6.31%	 16.81%	 13.88%

carbon [15,16] and the widened diffraction peaks are attributed to the amorphous phase of MC. The Ni-Ga peaks are shown at 35.20°, 44.18°, 64.40° for $NiGa_3$/MC [5]; 35.20°, 44.18°, 64.40° for NiGa/MC [4], and 43.49°, 50.71°, 74.55° for Ni_5Ga_3/MC [4–6]. Ni_5Ga_3/MC shows good crystallinity. The indication of partial oxidation in NiGa and $NiGa_3$ can be observed at 2θ = 31.67° (JCPDS No 11-0370), which is a footprint of small gallium oxide formation [17]. Moreover, the peak at 30.10° in NiGa and $NiGa_3$ is attributed to Ga(0) reported at PDF No 05-0601 [18]. As a comparison, Ga/MC exhibited 2θ at 30.10°, 64.57° that corresponds to the presence of Ga(0), and peaks at 31.67° and 35.37° for Ga_2O_3 [17]. For Ni/MC, diffraction peaks at 44.69° (111), 51.72° (200), 76.3° (220) corresponding to Ni(0), based on PDF No.04-0850 [10,19].

The morphologies and elemental composition of MC, Ni/MC, Ga/MC, $NiGa_3$/MC, NiGa/MC, and Ni_5Ga_3/MC were investigated by SEM-EDS, as shown in Figure 3. The MC shows a smooth morphology, both Ni/MC and Ga/MC present rough surfaces. $NiGa_3$/MC, NiGa/MC, and Ni_5Ga_3/MC show a slightly rough surface with white dots, corresponding to the impregnated metal into and/or spread out on the MC surface. The results of mapping and elemental composition are summarized in Table 2. The concentration of carbon in parent MC is 98.89%, then after metal impregnation,

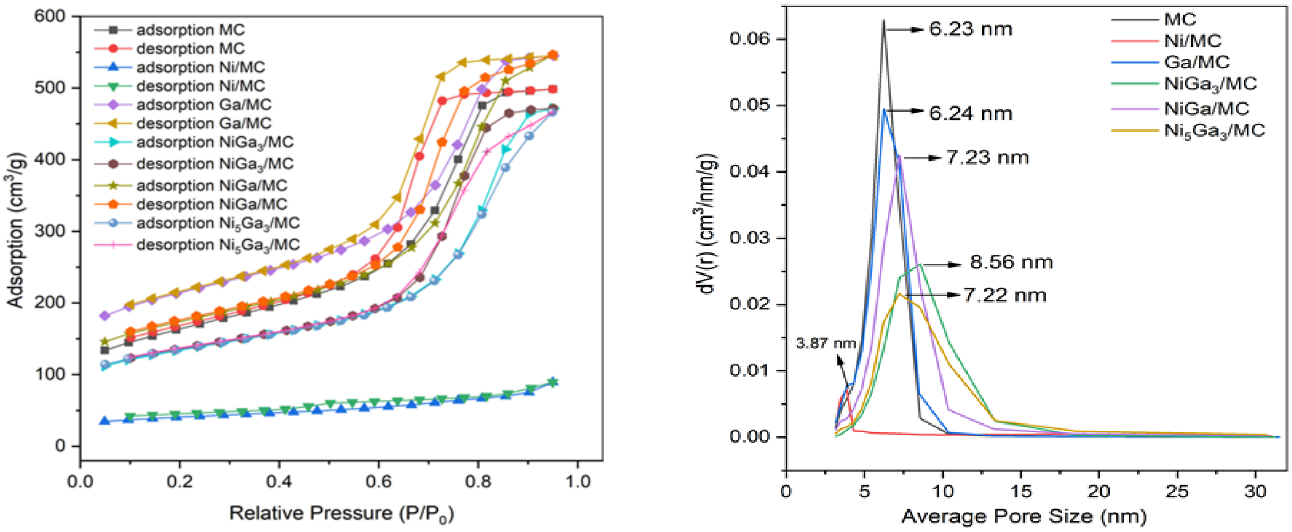


Figure 4. Surface area analysis of prepared material, (a) N_2 adsorption-desorption isotherm and (b) pore size distribution.

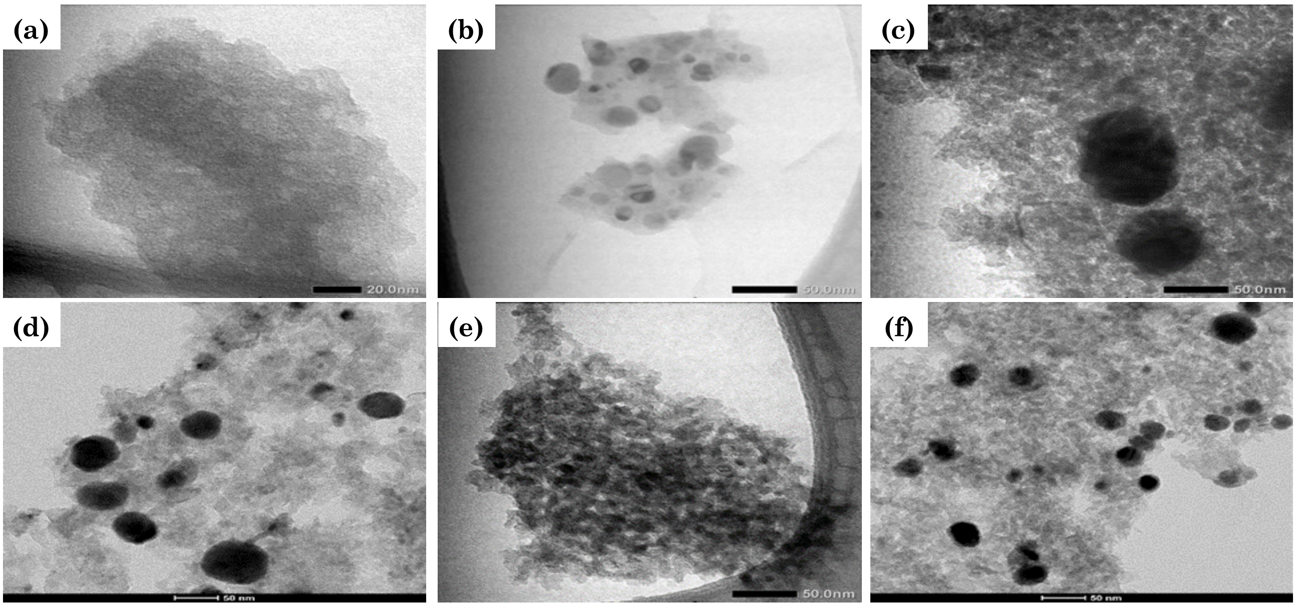


Figure 5. TEM image of prepared material (a) MC, (b) Ni/MC, (c) Ga/MC, (d) $NiGa_3$/MC, (e) NiGa/MC, and (f) Ni_5Ga_3/MC.

it decreased to 52.06–77.44% while the number of metals was detected. This phenomenon indicates the successful impregnation of the metal in MC.

Figure 4 shows the BET-SAA analysis on MC and MC-supported Ni-Ga catalysts. The N_2 adsorption-desorption isotherms of all materials exhibit the isotherm type IV, a distinct hysteresis loop points to mesoporosity in the materials. The average pore size distribution of support and the series of catalysts investigated by the BJH method show mesoporous material characteristics (2 – 50 nm). A remarkably large surface area of MC (599.00 m^2/g) was obtained in this study, which then decreased after modification in Ni/MC (139 m^2/g), $NiGa_3/MC$ (446 m^2/g), and Ni_5Ga_3/MC (456 m^2/g), indicating that metals have successfully impregnated to the channel of MC. On the other hand, the surface area of Ga/MC (699 m^2/g) and NiGa/MC (571 m^2/g) were larger than the parent MC, suggesting that the impregnated metals also resided on the surface of MC to form new nanoclusters. TEM analysis on the catalysts (Figure 5) support this finding. The parent MC shows a worm-hole-like structure [14], while in the Ni/MC, the metals (Figure 5(b)) are well dispersed into the pores (blackish spots), while in Ga/MC (Figure 5(c)), the metals grow as nanoclusters outside the surface. Interestingly, in $NiGa_3/MC$ and Ni_5Ga_3/MC catalysts, the metals grow inside and outside the pores. The profile of NiGa/MC is somewhat similar to that of Ga/MC. All catalysts show the metal size ranging less than 10 nm.

3.2 Catalyst Activity Test

Since the Ni_5Ga_3/MC catalyst shows superior physicochemical properties than other as-prepared catalysts (*e.g.* well-formation and well-dispersed metals on the support, high crystallinity, and large surface area), it was used to optimize the condition of the catalytic reaction of CO_2 reduction. The catalyst activity was determined from the conversion of CO_2, yield (μmol/g), and product selectivity. Based on the analysis of the reaction products using GC-FID, it is known that formaldehyde is the major product of the CO_2 hydrogenation reaction, accompanied by the presence of small amounts of methanol. Figure 6 shows the effect of the working temperature on the reaction. The highest conversion of CO_2 and the yield of formaldehyde (10.80% and 588 μmol/g) are observed at the reaction at 200 °C, while in the reaction occurring below 200 °C, the energy given is not enough to initiate the reaction; at over 200 °C, the reaction direction returns to the reactants. This is related to the exothermic reaction of CO_2 hydrogenation ($\Delta H_{298K} = -49.5$ kJ/mol to methanol and −42.55 kJ/mol to formaldehyde). As suggested by Zhou *et al.* [20] that the hydrogenation reaction of CO_2 took place following the mechanism pathways: CO_2 will be consecutively reduced to formic acid, formaldehyde, methanol and methane.

At the optimum reaction temperature, 200 °C, the catalyst activity test was carried out using MC, Ni/MC, Ga/MC, NiGa/MC, $NiGa_3/MC$, and the results are exhibited in Figure 7. MC was proven to be an inactive catalyst with the low conversion of CO_2 due to adsorption on the mesoporous carbon surface. All other tested

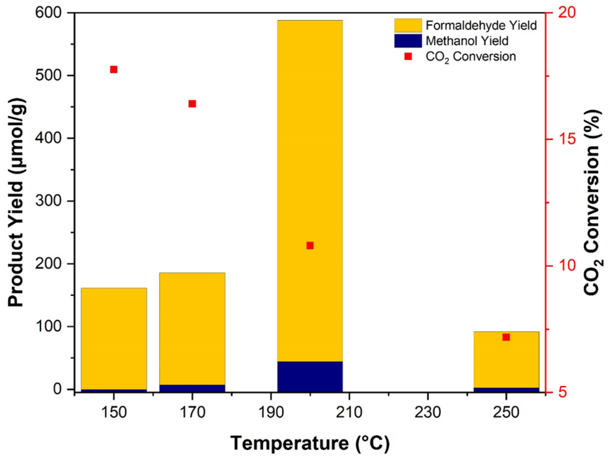


Figure 6. Temperature screening for CO_2 hydrogenation using Ni_5Ga_3/MC catalyst. Reaction condition P = 1 atm, $H_2:CO_2$ molar ratio = 3:1, T = 150–250 °C.

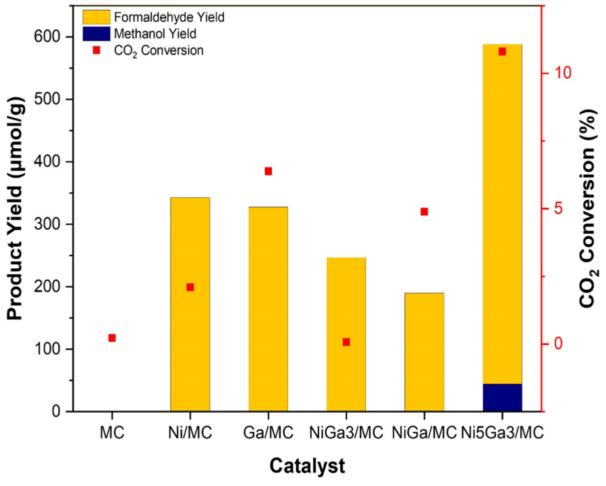


Figure 7. CO_2 hydrogenation over prepared catalysts. Reaction condition P = 1 atm, $H_2:CO_2$ molar ratio = 3:1, T = 200 °C.

catalysts show 100% formaldehyde selectivity, except for Ni_5Ga_3/MC (588 µmol/g formaldehyde, 44.38 µmol/g methanol or 93% formaldehyde selectivity). Among the three Ni-Ga catalysts, Ni_5Ga_3/MC provides the highest CO_2 conversion and product yield. Likewise, when compared with monometallic catalysts (Ni/MC and Ga/MC). This result is related to the catalyst characteristics as previously described that Ni_5Ga_3/MC has a good crystallinity of the δ-Ni_5Ga_3/MC phase, which has been previously reported as the active Ni-Ga phase on CO_2 hydrogenation. In addition, Ni_5Ga_3/MC also has a high surface area with a uniform metal distribution as previously shown in SAA-BET results in Figure 4 and TEM image in Figure 5. In term of pore size and distribution, the Ni_5Ga_3/MC catalyst also shows a wide pore size with a uniform distribution within the range of 5–13 nm with an average pore size of 7.22 nm. These properties support its good catalytic activity in converting CO_2 to formaldehyde and methanol even at ambient pressure. The catalytic test also showed that when in the right ratio (*i.e.* 5:3), Ni and Ga gave a synergistic effect that increased product formation, in which the Ni_5Ga_3/MC catalyst gave formaldehyde yields almost twice the formaldehyde yields given by monometallic Ni/MC or Ga/MC catalysts.

The CO_2 hydrogenation reaction mechanism on a Ni-Ga/MC catalyst is shown in Figure 8. According to Ahmad & Upadhyayula [7], the catalyst's active site, either Ni or Ga, has a critical role in this CO_2 hydrogenation. This catalyst can activate both CO_2 and H_2 so that these two substrates are ready to interact under mild conditions.

4. Conclusions

The mesoporous carbon synthesized using a soft-template with phloroglucinol as a carbon precursor and pluronic F-127 as a template has good characteristics to support Ni-Ga catalysts. Ni-Ga/MC catalyst was successfully synthesized using the impregnation method by H_2 reduction at 700 °C for 2 hours. The hydrogenation reaction of CO_2 on the Ni_5Ga_3/MC catalyst shows ~100% selectivity to formaldehyde, with the highest yield obtained at 200 °C. Increasing the temperature reaction above 200 °C results in a decrease in CO_2 conversion, corresponding to the exothermic reaction conditions. Herein, both Ni and Ga metals show an important role in the CO_2 hydrogenation. In Ni_5Ga_3/MC catalyst, the formation of formaldehyde and methanol products indicates the critical key of bimetallic Ni_5Ga_3 alloy formation in the application of CO_2 hydrogenation.

Acknowledgment

The authors gratefully acknowledge FMIPA Universitas Indonesia for FMIPA Universitas Indonesia Research Grant contract number NKB-017/UN2.F3/HKP.05.00/2021 for funding this project and Afif Z. Pamungkas for setting up the catalyst reactor.

References

[1] Rafiee, A., Khalilpour, K.R., Milani, D., Panahi, M. (2018). Trends in CO_2 conversion and utilization: A review from process systems perspective. *Journal of Environmental Chemical Engineering*, 6(5), 5771–5794. DOI: 10.1016/j.jece.2018.08.065.

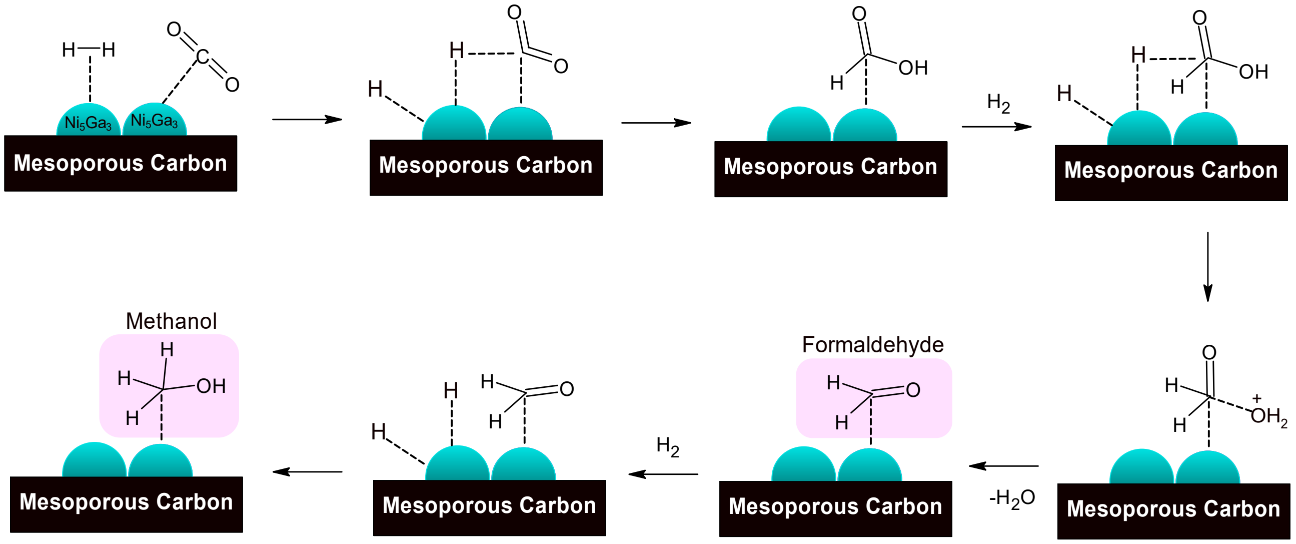


Figure 8. The proposed CO_2 hydrogenation mechanism reaction on Ni-Ga/MC catalyst.

[2] Alper, E., Orhan, O.Y. (2017). CO_2 utilization: Developments in conversion processes. *Petroleum*, 3(1), 109–126. DOI: 10.1016/j.petlm.2016.11.003.

[3] Krajčí, M., Hafner, J. (2016). Intermetallic compounds as selective heterogeneous catalysts: insights from DFT. *ChemCatChem*, 8(1), 34–48. DOI: 10.1002/cctc.20150073.

[4] Studt, F., Sharafutdinov, I., Abild-Pedersen, F., Elkjær, C.F., Hummelshøj, J.S., Dahl, S., Chorkendorff, I. Nørskov, J.K. (2014). Discovery of a Ni-Ga catalyst for carbon dioxide reduction to methanol. *Nature Chemistry*, 6(4) 320–324. DOI: 10.1038/nchem.1873.

[5] Nguyen, H.K.D., Dang, T.H., Nguyen, N.L.T., Nguyen, H.T., Dinh, N.T. (2018). Novel Ni-Ga alloy based catalyst for converting CO_2 to methanol. *The Canadian Society for Chemical Engineering*, 96(4), 832–837. DOI: 10.1002/cjce.23006.

[6] Ahmad, K., Upadhyayula, S. (2019). Conversion of the greenhouse gas CO_2 to methanol over supported intermetallic Ga–Ni catalysts at atmospheric pressure: thermodynamic modeling and experimental study. *Sustainable Energy & Fuels*, 3(9), 2509–2520. DOI: 10.1039/c9se00165d.

[7] Ahmad, K., Upadhyayula, S. (2020). Kinetics of CO_2 hydrogenation to methanol over silica supported intermetallic Ga_3Ni_5 catalyst in a continuous differential fixed bed reactor. *International Journal of Hydrogen Energy*, 45(1), 1140–1150. DOI: 10.1016/j.ijhydene.2019.10.156.

[8] Jiang, X., Nie, X., Guo, X., Song, C., Chen, J. G. (2020). Recent advances in carbon dioxide hydrogenation to methanol via heterogeneous catalysis. *Chemical Reviews*, 120(15), 7984–8034. DOI: 10.1021/acs.chemrev.9b00723.

[9] Liang, C., Li, Z., Dai, S. (2008). Mesoporous carbon materials: synthesis and modification. *Angewandte Chemie International Edition*, 47(20), 3696–3717. DOI: 10.1002/anie.200702046.

[10] Amelia, I., Krisnandi, Y.K., Abdullah, I. (2020). Synthesis and characterization of soft and hard templated mesoporous carbon using phloroglucinol as carbon precursor. *IOP Conference Series: Materials Science and Engineering*, 902(1), 012023. DOI: 10.1088/1757-899X/902/1/012023.

[11] Khairani, N.S., Abdullah, I., Krisnandi, Y.K. (2020). Synthesis and characterization of NiZn/mesoporous carbon as heterogeneous catalyst for carboxylation reaction of acetylene with CO_2. *AIP Conference Proceedings*, 2242(1), 040039. DOI: 10.1063/5.0007890.

[12] Kawigraha, A.D.H., Krisnandi, Y.K., Abdullah, I. (2020). Synthesis of impregnated nickel-mesoporous carbon and its application for reaction of acetylene with carbon dioxide. *IOP Conference Series: Materials Science and Engineering*, 763(1), 012040. DOI: 10.1088/1757-899X/763/1/012040.

[13] Abdullah, I., Andriyanti, R., Nurani, D.A., Krisnandi, Y.K. (2021). Nickel-phenanthroline Complex Supported on Mesoporous Carbon as a Catalyst for Carboxylation under CO_2 Atmosphere. *Bulletin of Chemical Reaction Engineering & Catalysis*, 16(1), 111–119. DOI: 10.9767/bcrec.16.1.9733.111-119.

[14] Gorka, J., Zawislak, A., Choma, J., Jaroniec, M. (2008). KOH activation of mesoporous carbons obtained by soft-templating. *Carbon*, 46(8), 1159–1161. DOI: 10.1016/j.carbon.2008.03.024.

[15] Chiou, J.Y., Kung, H.Y., Wang, C.B. (2017). Highly stable and active Ni-doped ordered mesoporous carbon catalyst on the steam reforming of ethanol application. *Journal of Saudi Chemical Society*, 21(2), 205–209. DOI: 10.1016/j.jscs.2015.10.006.

[16] Ortega-Franqueza, M., Ivanova, S., Domínguez, M.I., Centeno, M.Á. (2021). Mesoporous Carbon Production by Nanocasting Technique Using Boehmite as a Template. *Catalysts*, 11(9), 1132. DOI: 10.3390/catal11091132.

[17] Kumar, S., Sarau, G., Tessarek, C., Bashouti, M.Y., Hähnel, A., Christiansen, S., Singh, R. (2014). Study of iron-catalysed growth of ß-Ga_2O_3 nanowires and their detailed characterization using TEM, Raman and cathodoluminescence techniques. *Journal of Physics D: Applied Physics*, 47(43), 435101. DOI: 10.1088/0022-3727/47/43/435101.

[18] Kumar, V.B., Mastai, Y., Porat, Z.E., Gedanken, A. (2015). Chiral imprinting in molten gallium. *New Journal of Chemistry*, 39(4), 2690–2696. DOI: 10.1039/c4nj02081b.

[19] Li, J., Li, P., Li, J., Tian, Z., Yu, F. (2019). Highly-dispersed Ni-NiO nanoparticles anchored on an SiO_2 support for an enhanced CO methanation performance. *Catalysts*, 9(6), 506. DOI: 10.3390/catal9060506.

[20] Zhou, J., Huang, L., Yan, W., Li, J., Liu, C., Lu, X. (2018). Theoretical Study of the Mechanism for CO_2 Hydrogenation to Methanol Catalyzed by trans-RuH_2(CO)(dpa). *Catalysts*, 8(6), 244. DOI: 10.3390/catal8060244.