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ABSTRACT
Novel Ni-Ga based catalysts including Ni-Ga alloy, Ni-Ga/mixed oxide and Ni-Ga/mesosilica were prepared through metal melting, co-condensation-evaporation and impregnation methods, respectively. These three methods, by the above order, were established at temperatures of 1500 °C for 3 hours, 70 °C for 24 hours and room temperature overnight, respectively. The activity of these catalysts were studied in methanol synthesis from CO2. Results showed that the Ni-Ga alloy, Ni-Ga/mixed oxides and Ni-Ga/mesosilica catalysts mostly contained the multiple crystal phases, the active sites of crystalline δ-Ni5Ga3 distributed on Ni-Ga mixed oxide, and the active sites of crystalline δ-Ni5Ga3 distributed on mesosilica support, respectively. The Ni-Ga/mesosilica catalyst showed the highest activity in the conversion of CO2 to CH3OH. The catalyst structures and properties were characterized by SAXRD, WAXRD, SEM, TEM and XPS techniques. Gas products were determined by GC coupled with either TCD or FID for inorganic or organic compound, respectively.

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I. INTRODUCTION
Methanol will play a key role in chemistry-petrochemistry industry in the near future because of its vast potentiality in many industrial processes. "Methanol Economy", a terminology proposed by George Olah, will be innovative and attractive in many sectors including fuel productions, storages, which could well and strongly compete with those derived from fossil resources (Felix et al., 2014; George et al., 2009; and Hansen and Nielsen, 2008).

Industrially, there were some processes producing methanol from syngas, methane, etc., which have been developing and yielding a vast amount of methanol each year. However, demand for methanol would be still much larger. Because most of the feedstock for the methanol production came from fossil resources including crude oil, coal, nature gas, they were strongly depended on the development and price of oil and gas industry. Actually, the fossil resources for methanol production would be restricted in near future when oil storage was decreased, so there were many drawbacks affecting the production of methanol in the future consisting of price, productivity and environmental impact (Behrens et al., 2012; Lim et al., 2009; Liu et al., 2003; Campbell et al., 1987; Cong et al., 2015; Irek et al., 2014; Suhas et al., 2014; Seiki et al., 2013; Ibiram, 2014; and Wang et al., 2011).

Scientifically, most of efforts in the productions of methanol mainly aimed to develop some aspects such as finding out alternative feedstock, inventing new processes and researching novel and advanced catalysts. Recently, one of the best feedstock has been mentioned as CO2 because of many reasons: it could be collected from many resources with unlimited and renewable amount; it could be directly synthesized from CO2 over suitable catalyst; and using it could effectively reduce greenhouse impact in the earth (Irek et al., 2014; Ibiram, 2014; and Wang et al., 2011). By the catalysis approaches, there were some traditional ones recently used in the methanol synthesis process including Cu/ZnO, ZnO/Cu (Suhas et al., 2014; Wu et al., 2001), Cu/ZnO/Al2O3 (Wu et al., 2001; Ma et al., 2009), Cu/ZnO/Al2O3/ZrO2 (Wu et al., 2001), and Pd...
based catalysts (Shen et al., 2001; Kim et al., 2003; Liang et al., 2009; and Iwasa et al., 2009); their activity and selectivity were illustrated. However, there were many issues which should be improved; i.e., they had to be activated at high temperatures and pressures, or they showed low selectivity of methanol and produced many by-products such as CO, methane, etc. According to one of recent reports, Ni-Ga based alloy catalyst varied by different Ni/Ga molar ratios have been tested in the methanol synthesis at milder pressure and temperature. The CO2 conversion and methanol selectivity were higher than those of other processes using other catalysts. The appearance of high active Ni5Ga3 site (Felix et al., 2014; Tremblay, 2008) provided many positive effects for the CO2 conversion. Therefore, the catalyst have attracted many scientific studies. However, many characteristics of the catalysts should be clarified, and the combinations of Ni and Ga metals in many states should be also tested for choosing the most effective candidate in the methanol synthesis.

The Ni-Ga alloy catalysts have been also an interesting topic for our studies recently. However, activity and selectivity of the alloy catalysts were not as good as being reported by other researches because of impurity and inhomogeneous distribution of Ni5Ga3 active site on the surface. Explanations also proved that the alloy stage was not good candidate for the conversion because of the above reasons. Two previous published works of us (Hong et al., 2018; Hong and Toan, 2019) mentioned characterizations of the Ni-Ga/mixed oxides and Ni-Ga/mesosilica catalyst, respectively. A test of their activity in the conversion of CO2 was also conducted. However, many comparisons between them and another catalyst (Ni-Ga alloy) on their differences in preparations, structure characterizations and activity were being in questions. Therefore, this report focused on further characterizations of the Ni-Ga catalysts including Ni-Ga alloy, Ni-Ga/mixed oxides (NiGa/NiO-Ga2O3 mixed oxide) and Ni-Ga/mesosilica (Ni-Ga supported on mesoporous amorphous silica). The most suitable catalyst for the conversion of CO2 to methanol would be chosen based on its structure, and then it was applied in the investigation of the methanol synthesis process.

II. EXPERIMENTAL

A. Chemicals

Chemicals applied in the study such as Ni(NO3)2.6H2O, HNO3 63% solution, Ga and Ni metals, NaOH, NaBH4, TEOs and CTAB were all purchased from Merck and could be used without any further purification. Distilled water was produced at the local lab through one-stage distillation.

B. Preparation of Ni-Ga based catalysts

1. Ni-Ga alloy catalyst

Ni-Ga alloy catalyst was prepared through metal melting method: Ni and Ga metals at molar ration of 5/3 were melted at 1500°C in an electrical oven under closed ceramic cup for 3 hours; the mixture in the cup was naturally cooled down to obtain Ni-Ga alloy catalyst.

2. Ni-Ga/mixed oxides catalyst

The Ni-Ga/mixed oxides catalyst were prepared through co-condensation-evaporation method using Ni(NO3)2.6H2O and Ga metal as precursors (Hong et al., 2018). Firstly, 2.1 g of Ga metal were completely dissolved in 100ml solution of HNO3 2M. The solution was homogeneously mixed with 50ml solution containing Ni(NO3)2. The molar ratios of Ni/Ga were controlled at 5/3. The prepared solution including metal cations but exceeding acid was neutralized and then precipitated by a suitable concentrated NaOH solutions under vigorous stirring until pH of the solution was 9.5±10. A heater was supported to increase the temperature of the mixtures to 70°C for 24 hours under non-refluxed condition. Therefore, the water solvent gradually evaporated, and the mixture after 24 hours became a gel state. The gel was then washed and filtered until the pH of the waste water was neutral. The cakes after the filtering were dried overnight at 100°C before being introduced to a calcination at 500°C for 6 hours obtaining Ni-Ga mixed oxide. The mixed oxide was reduced for 5 hours in 100 ml ethanol solution containing 2.0 g of NaBH4 for partially converting the mixed oxide to alloy/mixed oxide mixture. The filtering and drying processes were finally applied to obtain Ni-Ga/mixed oxides catalyst.

3. Ni-Ga/mesosilica catalyst

The Ni-Ga/mesosilica catalyst was prepared through impregnation method; in which, nitrates of Ni31+ and Ga31+ were impregnated on mesosilica support (Hong and Toan, 2019). Firstly, the mesosilica support was prepared through condensation method: 4.0 g NaOH was dissolved in 50 ml deionized water to produce NaOH 2M solution; 3.5 ml of the NaOH 2M solution was dropped into 460 ml deionized water to prepare NaOH ∼ 0.015M solution (solution A); 150 ml solution A was then transferred into rounded bottle supported with reflux condenser, magnetic stirrer and heater; the stirring speed was kept at 500 rpm while gradually adding 2 g CTAB into the solution; after completely dissolving CTAB, raising the temperature of the solution to 90°C as well as adding a volume of 10 ml TEOs into the solution (pouring speed of 0.5 ml/min); pH value of the solution after adding all the chemicals should be controlled to be 10 by drop-wise supplying a dilute NaOH solution (0.2M); the condensation was established under refluxed condition for 24 hours followed by separating the precipitate from the solution; the precipitate was washed and filtered using distilled water followed by being dried at 110°C overnight and calcinated at 550°C for 4 hours to obtain the mesosilica.

Secondly, the impregnation of nitrates over mesosilica support was carried out: 2 g of Ni(NO3)2 and Ga(NO3)3 with Ni/Ga molar ratio of 5/3 was dissolved in 30-50 ml distilled water followed by adding to the solution 5g of the as-synthesized mesosilica; the mixture was well mixed under ambient temperature and pressure in a closed cup for 24 hours; the mixture was then transferred to a evaporating dish for drying; the solid was homogeneously ground and applied to a calcination process at 500°C for 3 hours in a crucible cup without lid; the calcinated product was then immersed into the NaBH4/ethanol solution with the same procedure as being established in the Ni-Ga/mixed oxides catalyst preparation.

C. Activity of catalysts in conversion of CO2 to methanol

Catalysis activity was tested by using a fixed-bed reactor made of quartz glass (internal diameter 6 mm). For the first procedure, the
catalyst would be re-activated by exposing it at 200 °C for 3 hours in H₂ atmosphere (flow rate of 30 ml/min).

After the re-activation, the methanol synthesis was carried out using feedstock as a mixture of H₂ and CO₂ (H₂/CO₂ volume ratio of 3/1). Total flow rate of the gase phase was fixed at 100 ml/min, while the volume of the catalytic bed was 1 ml yielding a gas hourly space velocity of 6000 h⁻¹. The conversion included two main followed reactions:

Main reaction: CO₂ + 3H₂ = CH₃OH + H₂O

Side reaction: CO₂ + H₂ = CO + H₂O

The outlet stream including many components as inconverted reactants, by-products and main products. They were all analysed with an Agilent 7890A gas chromatography (GC), coupled with thermal conductivity detector (TCD) and flame ionization detector (FID) for analysis of inorganic and organic compounds, respectively. Temperature and pressure of the conversion were fixed at 220 °C and 30 bars, respectively. Gas sample was periodically collected each 1 hour for the analysis, and 5 to 7 measurements were taken at each collecting time and for calculating the gas composition. Activity and selectivity of CO₂ and methanol were calculated by these compositions.

D. Characterizations

The catalyst was characterized by XRD, SEM, TEM and XPS methods. Powder XRD was recorded on a D8 Advance Bruker diffractometer using Cu Kα (λ = 0.15406) radiation. SEM images were recorded on Field Emission Scanning Electron Microscope S – 4800. TEM images were captured on JEM1010-JEOL TEM operated at energy of 80 kV. XPS measurements were performed using a Ulvac PHI spectrometer fitted with a monochromatic Al (1486.7 eV) X-ray source. The area analyzed was ~400 × 400 μm². Finally ground powders were pressed into In foil and mounted on an electrically grounded sample holder. The In 3d core level spectrum was measure to be sure no signal from indium foil was detected. High-resolution spectra of the Mg 2s, Al 2p, K 2p, Co 2p3, Ni 2p3, Ga 3d, Si 2p, Si 2s, O 1s, and C 1s core lines were collected with a pass energy of 58 eV, a step size of 0.1 eV, and a sweep time of 240s. To counter differential charging, the charge neutralizer was used during collection of spectra. During data analysis, the samples were calibrated using the C 1s line arising from adventitious C with a fixed value of 284.8 eV. A Shirley-type function was applied to remove the background arising from energy loss. Gas composition was investigated by GC (Thermo Finnigan Trace GC Ultra) coupled with TCD and FID for inorganic and organic compounds, respectively.

III. RESULTS AND DISCUSSIONS

A. X-ray diffractions (XRD)

Crystalline properties of the catalysts were characterized by Wide Angle X-Ray Diffraction technique (WAXRD). They were all plotted in Figure 1.

The WAXRD pattern of the Ni-Ga alloy catalyst showed a complicated system of peaks assigned for co-existence of many crystal phases including NiO, Ga₂O₃, Ni and Ga metals at corresponding 2theta values of ~12°; 15°; 18°; 20°. . . . The catalyst contained many impurities beside the desired active phase (Ni₅Ga₃) which appeared at 2theta ~ 36°, 43°, 50°, 62° (Felix et al., 2014; Ibram, 2014). The active sites in the catalyst were mixed with many other components (Felix et al., 2014; Ibram, 2014). Therefore, although the crystallinity of the Ni-Ga alloy catalyst could be considered the highest compared to the others (based on the height ratio between the specific peak and the background), the purity of the catalyst was not good (Felix et al., 2014; Cong et al., 2015).

The WAXRD patterns of the Ni-Ga/mixed oxides and Ni-Ga/mesosilica catalysts, in contrast to that of the Ni-Ga alloy, showed only δ-Ni₅Ga₃ crystal phase and amorphous silica background proving its high purity of the crystal active sites. The intensity of the background was high in both catalysts indicating that they contained a large content of amorphous support. The high crystalline purity of the active site δ-Ni₅Ga₃ was a good signal
FIG. 3. SEM images of Ni-Ga based catalysts.

for its ability of application in the methanol synthesis. The crystallinity of the Ni-Ga/mixed oxides was higher than that of the Ni-Ga/mesosilica.

Although the Ni/Ga molar ratio in the precursors was the same, the WAXRD patterns showed considerable different structures for each catalyst. Explanation could be based on the different preparation procedure of each one: the metal melting method applied an extremely high temperature (1500°C) which led to generate many by-products beside the desired sites of $\delta$-Ni$_5$Ga$_3$; in the Ni-Ga/mixed oxides and Ni-Ga/mesosilica, the calcinations and reductions were established at much lower temperature, so the by-products were hardly formed yielding the most popular crystal phase of $\delta$-Ni$_5$Ga$_3$.

The crystallinity of the Ni-Ga/mixed oxides was higher than that of the Ni-Ga/mesosilica because of their different preparation method and composition: in which, the reduction of the
Ni-Ga/mixed oxides could be partially conducted to generate the $\delta$-Ni$_5$Ga$_3$ sites distributed on the mixed oxides of NiO and Ga$_2$O$_3$ while the impregnation and reduction of the Ni-Ga/mesosilica mostly produced the $\delta$-Ni$_5$Ga$_3$ phase distributed on the amorphous mesoporous silica; the content of the support in the Ni-Ga/mesosilica catalyst was higher than that of the Ni-Ga/mixed oxides also importantly contributed to the difference in their crystallinity. The mesosilica support in the Ni-Ga/mesosilica catalyst could possibly played a crucial role in the distribution of the $\delta$-Ni$_5$Ga$_3$ active site over the catalysts surface which would strengthen its stability and activity in the methanol synthesis.

Figure 2 plotted Small Angle X-Ray Diffraction (SAXRD) patterns of the catalysts and mesosilica support to characterize the short-range order property of these materials.

Results extracted from the patterns probably indicated that there was no trace of the ordered mesoporous structure in the Ni-Ga and Ni-Ga/mixed oxides, but in it was obviously clear in the Ni-Ga/mesosilica catalyst. The SAXRD pattern of the Ni-Ga/mesosilica catalyst and the mesosilica support clearly exhibited the existence of finger print peaks at 2theta ~2° and ~4° corresponding to (100) and (110) reflection planes in a typical ordered mesoporous material (Wanger et al., 1979; Hong et al., 2017a; 2017b; and Hong and Toan, 2017c). Intensity of the major peak at 2theta ~2° just slightly decreased from the mesosilica to the catalyst indicating the good stability of the mesoporous channels during the catalyst preparation and the good dispersion of the $\delta$-Ni$_5$Ga$_3$ active site on the surface (Irek et al., 2014).

B. Morphology of Ni-Ga based catalysts

Figure 3 and 4 described SEM and TEM images of the catalysts. As being observed in the SEM images, the Ni-Ga alloy catalyst showed crystalline surface containing large crystalline particles generated by agglomerations of small clusters of the different compounds relating to Ni and Ga during the preparation at extreme temperature (1500 °C). These particles had ununiform sizes attaching together corresponding to a poor dispersion of the active site. The Ni-Ga/mixed oxides catalyst, in contrast, majorly included adjacent spherical likely particles having sizes ranged from 28-70 nm yielding a better porous structure than in the Ni-Ga alloy catalyst. The porous structure of this catalyst could be assigned for the existence of the mentioned Ni-Ga mixed oxides. The SEM images of the Ni-Ga/mesosilica catalyst contained many uniform particles having sizes of ~20-42 nm which could be considered as the catalyst with the highest porosity.

As shown in Figure 4, TEM images of these catalysts also indicating that the Ni-Ga alloy, Ni-Ga/mixed oxides and Ni-Ga/mesosilica catalysts clearly possessed dense structure with low porosity, tiny particles inside each large one, and ordered mesoporous channels inside each particle, respectively. The mesoporous channels had a high degree of order. These results well agreed with the observations and analysis from the WAXRD, SAXRD and SEM results. The results obtained from the SEM and TEM images could be also easily understandable when considering the different preparation methods of these catalysts.

There were some important points which could be noted when inspecting the properties of these catalysts through their structure and morphology characterizations: the Ni-Ga alloy catalyst had the highest crystallinity, but the lowest content of the $\delta$-Ni$_5$Ga$_3$ active site caused by the metal melting preparation; the Ni-Ga/mixed oxides catalyst had good purity of the $\delta$-Ni$_5$Ga$_3$ active sites, good crystallinity, but not possessing an ordered mesoporous system; the Ni-Ga/mesosilica had high purity of the $\delta$-Ni$_5$Ga$_3$ active site, low crystallinity because of high percentage of amorphous mesosilica support and contained ordered mesoporous channels built by stable silica walls. Therefore, the Ni-Ga/mesosilica catalyst could be considered as the best candidate for enhancing the distribution of the $\delta$-Ni$_5$Ga$_3$ active sites. As a consequence, the Ni-Ga/mesosilica catalyst was choosen for its potential of having high activity in the methanol synthesis. XPS analysis was established with this catalyst to illustrate its chemical element states.
C. X-ray photoelectron spectroscopy (XPS) analysis for Ni-Ga/mesosilica catalyst

The chemical state of the Ni-Ga/mesosilica catalyst plotted for whole bands and for each element including Ni, Ga, O, C and Si was analyzed by XPS technique and exhibited from Figure 5 to Figure 12; these important elements appeared as peaks at \( \sim 855 \text{ eV}, 1118 \text{ eV}, 531 \text{ eV}, 282 \text{ eV} \) and \( 102 \text{ eV} \), respectively \((\text{Wanger et al.}, 1979)\). Percentage for Ni and Ga cores – the most important elements were also calculated.

According to the analysis, the catalyst contained Ni, Ga, O and Si elements; in which Ni and Ga were the most important ones \((\text{Wanger et al.}, 1979)\). The results plotted for Ni and Ga also confirmed that there were a partial amount of Ni and Ga based cations being reduced in the NaBH4 environment. For example, 22.47\% of the Ga\(^{3+}\) cation was converted to Ga in the allow \( \delta \)-Ni\(_3\)Ga\(_3\) (active sites of the catalyst), and 66.95\% of Ni\(^{2+}\) did the same process becoming Ni in the active phase.

The XPS spectra also well demonstrated the existence of the \( \delta \)-Ni\(_3\)Ga\(_3\) active sites with corresponding binding energies of each elements, and the results also probably adaptable with the analysis of the previous SAXRD and WAXRD patterns.

D. Activity of Ni-Ga/mesosilica catalyst in methanol synthesis from CO\(_2\)

The most important component of the conversion was CH\(_3\)OH and CO\(_2\), so the conversion and selectivity of the CO\(_2\) and methanol, respectively, were used to test the activity of the Ni-Ga/mesosilica
FIG. 11. Quantification of Ga core in Ni-Ga/mesosilica catalyst.
FIG. 12. Quantification of Ni core in Ni-Ga/mesosilica catalyst.
catalyst. Figure 13 and Table I exhibited investigation results by time of the conversion.

Results obtained from the conversion clearly showed high activity and selectivity of the Ni-Ga/mesosilica catalyst, both in converting CO\(_2\) and in selecting main product (methanol). The conversion of CO\(_2\) and the selectivity of methanol slightly decreased by the time also indicated that the catalyst was stable at the reaction conditions: the CO\(_2\) conversion at the beginning reached relatively high value of 36.8%; then it gradually reduced to a stable value after 14 hours; the changing of the methanol selectivity was the same.

The high activity of the Ni-Ga/mesosilica catalyst could be assigned for nature of the δ-Ni\(_5\)Ga\(_3\) active phase (Felix et al., 2014): the crystal phase at high temperature could exhibit the same characteristic of type n semi-conductors producing electrons inside the alloy system. Therefore, these electrons and "positive holes" could elastically move through the alloy like structure of the active site’s structure, which dramatically enhanced the decomposition of surface-adsorbed H\(_2\) molecules to H atoms located on Ni positions. Ni moieties played as semi-hydrogenation sites instead of total-hydrogenation ones as proved in Pt sites in many other materials. The H atoms connected to Ni moieties became very active with the reduction of CO\(_2\) to many products. Besides, the CO molecules could be strongly adsorbed on the catalyst surface (Felix et al., 2014) weakening the π-bonding of the CO\(_2\) molecules. As a consequence, the selectivity for CO\(_2\) being reduced to methanol considerably increased. Otherwise, mesosilica also possessed well-distributed porous channels that increased the distribution of the active sites on the catalyst surface, and inhibited agglomeration of these sites under the process conditions.

For comparisons, conversion of CO\(_2\) and selectivity of methanol in CO\(_2\) reduction process over Ni-Ga and Ni-Ga/oxide catalysts were also exhibited along with the results obtained from the reduction process over Ni-Ga/mesosilica catalyst. Figure 14 and Figure 15 showed these analysis results.

The results obtained from analysis in Figure 14 clearly showed that the highest selectivity of methanol was achieved when the reduction process was conducted over Ni-Ga/mesosilica catalyst. At the lower levels of the selectivity were the processes carried out over Ni-Ga/oxide and Ni-Ga alloy catalysts, and this was well adaptable with the characterizations of these catalysts. The stability of the

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**TABLE I.** Conversion of CO\(_2\) and selectivity of methanol by time in methanol synthesis.

| Time, h | Methanol selectivity, % | CO\(_2\) conversion, % |
|--------|-------------------------|------------------------|
| 1      | 42.7                    | 36.8                   |
| 2      | 42.3                    | 36.5                   |
| 3      | 41.8                    | 36                     |
| 4      | 41.8                    | 35.7                   |
| 5      | 41.4                    | 34.8                   |
| 6      | 41.4                    | 34.4                   |
| 7      | 41.4                    | 34                     |
| 8      | 40.5                    | 33.6                   |
| 9      | 40                      | 32.2                   |
| 10     | 40                      | 31                     |
| 11     | 39.6                    | 30.6                   |
| 12     | 38.7                    | 30.1                   |
| 13     | 38.2                    | 29                     |
| 14     | 37.8                    | 28.5                   |
| 15     | 37.8                    | 28.4                   |
| 16     | 38.2                    | 28.3                   |
| 17     | 37.3                    | 28.1                   |
| 18     | 37.8                    | 28                     |
| 19     | 37.3                    | 28                     |
| 20     | 36.9                    | 28                     |
| 21     | 36                      | 27.7                   |
| 22     | 36                      | 27.8                   |
| 23     | 34.6                    | 27.6                   |
| 24     | 35.1                    | 27.7                   |
selectivity index also illustrated that the Ni-Ga/mesosilica catalyst was more suitable for the reduction of CO₂. The results obtained from Figure 15 also confirmed and demonstrated that the Ni-Ga/mesosilica catalyst was the best candidate for the methanol synthesis from CO₂ when showing a high and stable conversion of CO₂ during all the time of the process.

IV. CONCLUSION

Successfully preparing and characterizing different structures of Ni-Ga based catalysts such as Ni-Ga alloys, Ni-Ga/mixed oxides and Ni-Ga/mesosilica; in which the Ni-Ga had the highest crystallinity, but the lowest purity; the Ni-Ga/mixed oxides had good crystallinity of the δ-Ni₃Ga₃ phase and the Ni-Ga/mesosilica had low crystallinity. The Ni-Ga/mesosilica also contained ordered mesoporous structure greatly improving distribution of the active site on the catalyst surface. XPS analysis also confirmed the appearance of the δ-Ni₅Ga₃ phase along with other elements of the mesosilica framework such as Si and O. Because of the good distribution of the δ-Ni₅Ga₃ active phase, the Ni-Ga/mesosilica catalyst could be very effective in the conversion of CO₂ to methanol.

Establishing the test of activity of the Ni-Ga/mesosilica catalyst in CO₂ conversion to methanol. The analyzed results were considerably good because of existence and distribution of δ-Ni₅Ga₃ active sites on ordered mesoporous channels of mesosilica support. The catalyst was also stable at the conversion conditions for a long time proving its high stability. Both conversion and selectivity of the CO₂ reduction over the two other catalysts were lower than those of the Ni-Ga/mesosilica catalyst, and this proved that the Ni-Ga/mesosilica was the better candidate for the methanol synthesis from CO₂.

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