

Study on preparation of advanced Ni-Ga based catalysts for converting CO₂ to methanol

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Summary

The paper covered preparations and characterisations of Ni-Ga based catalysts including Ni-Ga alloy, Ni-Ga/mixed oxides, Ni-Ga/mesosilica and Ni-Ga-Co/mesosilica for synthesis of methanol from direct reduction of CO₂ under hydrogen. The Ni-Ga alloy and Ni-Ga/mixed oxides were prepared by metal melting method established at 1500°C and co-condensation-evaporation method at 80°C for 24 hours, respectively. The Ni-Ga/mesosilica and Ni-Ga-Co/mesosilica catalysts were both prepared by wet impregnation method at room temperature for 24 hours. The dried white powders obtained from the co-condensation-evaporation and the impregnation procedures were contacted with NaBH₄/ethanol solution for reducing metal cations to alloy state at room temperature. Investigations on conversion of CO₂ showed that the Ni-Ga/mesosilica and the Ni-Ga-Co/mesosilica catalysts behaved as the best candidates for the process when showing its high conversion of CO₂ and selectivity of methanol at high pressure of 35 bars. Especially, the Ni-Ga-Co/mesosilica showed considerable activity and selectivity in the process established at a low pressure of 5 bars. Techniques such as Small Angle X-Ray Diffraction (SAXRD), Wide Angle X-Ray Diffraction (WAXRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Fourier Transform - Infrared Spectroscopy (FT-IR) and X-Ray Photoelectron Spectroscopy (XPS) were applied for characterising the catalysts, and Gas Chromatography (GC) coupled Thermalconductivity detector (TCD) and Flame ionized detector (FID) were used for determining the gas reactants and products.

Key words: methanol, Ni-Ga, Ni-Ga-Co, carbon dioxide, methanol economy, mesoporous material.

1. Introduction

1.1. Methanol role and catalysis for converting CO₂ to methanol

Methanol is the simplest alcohol which can be easily stored, transported and used. Using methanol as a precursor for industrial chemistry processes has been estimated as one of the most important directions for the development of the chemical economy today. Methanol, as a fuel and precursor for organic synthesis, possesses some advantages: high octane rate (107 - 115) for gasoline blending, effective compound in fuel cell, good precursor in dimethyl ether production, high cetane number (55) for diesel additive, an important source for olefin production, then for most chemicals in cosmetic and industrial substances. Therefore, the "methanol economy" terminology would be declared by

many scientists and industrialists, based on its uses as a fundamental chemical for most products in the chemical economy [1 - 4].

Besides having been mainly produced from syn-gas containing CO and H₂, methanol could be synthesised from many other processes such as methane oxidation and CO₂ reduction, etc. The reduction of CO₂ to methanol has been considered as one of the greenest processes because CO₂ could be obtained from many sources including waste gases, atmosphere and natural sources. Therefore, synthesis of methanol from CO₂ would well contribute not only to industry, but also to environmental protection [1, 2, 5 - 7].

Recently, the synthesis of methanol has required very high pressure (50 - 100 bars), high temperature, over supported metal catalysts including Cu/ZnO/Al₂O₃. These processes produce methanol at low selectivity because of competition of CO generation. To overcome this drawback, catalysts applied for the conversion of

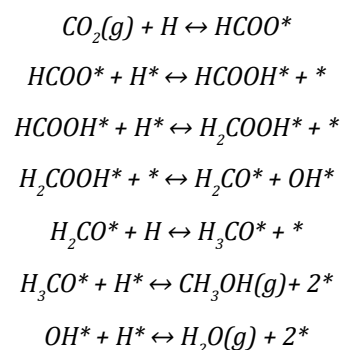
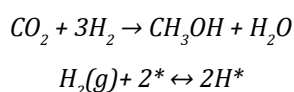
CO₂ would have high activity and selectivity at milder temperature and pressure [8 - 10].

The recent developments on the catalysts in the conversion of CO₂ to methanol have revealed Ni-Ga alloy based materials as one of the most active and effective candidates. Within a precise composition of the Ni-Ga alloy (Ni₅Ga₃), the activity and selectivity of the catalyst could be much stronger than other published ones at much milder temperature and pressure [8, 9]. According to the researches, the activity and selectivity of the Ni-Ga alloy could surpass most existing supported metal catalysts based on Zn, Cu, Pd and Pt, etc. However, they also confirmed that the selectivity of methanol could be further improved.

From our approaching points of view, both activity and selectivity of the Ni-Ga based catalyst could be strongly improved by enhancing its active site (Ni₅Ga₃) distribution over various types of support including increasing its specific surface area and strengthening its porous texture. By this orientation, we gradually developed many types of Ni-Ga based catalyst due to their increase in the distribution of the active site, consisting of Ni-Ga alloy, Ni-Ga/mixed oxides and Ni-Ga/mesoporous silica. An important realisation obtained after testing these kinds of catalysts was that their activity and selectivity sharply reduced for a period of time. It was caused by coagulation of the Ni₅Ga₃ active sites under the process conditions. Therefore, improving the active site distribution was not enough to stabilise the catalysis effectiveness. In this situation, metal promoters could be an important factor for stabilising the catalytic activity and selectivity through bridge connection between the supports and the active sites. Further studies led to preparation of Ni-Ga-Co/mesoporous silica catalyst where Co was introduced to the catalyst's composition. The reason for this development, as mentioned above, could be assigned to the bonding connection between Co and Ni and the supports avoiding the coagulation of Ni₅Ga₃ active sites during the conversion.

1.2. Mechanism of methanol synthesis from CO₂

Total reaction and mechanism for converting CO₂ to methanol could be described according to Behrens et al [10], where * symbol indicates an active site located on the catalyst surface; e.g. H* is considered as hydrogen atom connected to the active site of the catalyst.



CO₂ possesses C element at the highest oxidation state leading to difficulty in its conversion to any type of products. Therefore, most CO₂ conversions require severe technology parameters such as pressure of hundred bars and temperature of 250 - 300°C. They are just two of the main reasons for the low development of methanol production from CO₂ and many efforts on improvement of catalysis and process should be conducted and established.

1.3. Multimetallic catalysis in conversion of CO₂ to methanol

Studies on hydrogenation of CO₂ for methanol synthesis and the applied catalysis were reported for many years. Liu et al [11], in 2003, published C/Pd catalyst as the first Pd based material which could be used in the process. In 2009, Lim et al [12] indicated that Cu, Zn, Cr and Pd could play a crucial role in the reduction of by-products such as CO and hydrocarbons. Among them, Cu/ZnO and Cu/ZnO/Al₂O₃ catalysts were well known because of its relatively high activity and selectivity, in which the Al₂O₃ support partially helped in strengthening the catalytic activity. Otherwise, Zr could also play as a promoter for improving the Cu distribution over the supports.

Copper based catalysts such as Cu/ZrO₂, Cu/ZnO/ZrO₂, Cu/ZnO/Ga₂O₃ and CuO/ZnO/Al₂O₃ were also studied and one of them became a commercial candidate (Cu/ZnO/Al₂O₃) during the 1960s. Nowadays, the active site of these catalysts was assigned to Cu [13 - 16]. Besides competition between methanol and CO products, the process carried out over these catalysts was considerably affected by the generation of water. The generated water would be adsorbed over the catalytic active sites limiting the contact between them and the reactants. Water also ignited the coagulation of the active sites because of the hydrothermal induction at high temperature [4]. Copper based catalysts promoted by B, V and Ga were also reported [17]. Sloczynsky et al [18], in 2003, published

an article relating to determining the effects of Mg and Mn as promoters for Cu on activity and adsorption characteristics of CuO/ZnO/ZrO₂ catalyst. There were also many other studies investigating different supported Cu and Zn based catalysts for the process at 240°C - 260°C and 2 - 6 Mpa [19 - 24]. However, the conversion of CO₂ and selectivity of methanol were not high enough, and there were still CO that quickly deactivated and poisoned the catalytic performance.

Pd based catalysts seemed to be effective in the reduction of CO₂ [25]; however, its activity and selectivity mainly depended on the applied supports [26] and preparation methods [27]. Many studies showed that the Pd based catalysts could raise the methanol selectivity to 60%, but the content of CO in the gas products was still high. Besides, the catalysis expense for these kinds of materials was too high compared to Cu based ones [28 - 32].

That was to say the high pressure and low methanol selectivity issues became the main disadvantages of the methanol synthesis. Therefore, the discovery of new catalysis generations became essential for further developments in the conversion of CO₂ to methanol [8, 41].

2. Experimental

2.1. Catalysis preparations

2.1.1. Preparation of Ni-Ga alloy catalyst

Ni-Ga alloy catalyst was prepared through metal melting method: Ni and Ga metals at a molar ratio of 5/3 were melted at 1500°C in an electrical oven under the closed ceramic cup for 3 hours. The oven was filled by nitrogen gas at a flow of 100 ml/min for avoiding the contact between the metal parts with oxidative agents. After finishing the melting process, the mixture in the cup was naturally cooled down to obtain Ni-Ga alloy catalyst in bulk mass. The bulk was then grinded to tiny particles suitable for using in the methanol synthesis process.

2.1.2. Preparation of Ni-Ga/mixed oxides catalyst

The Ni-Ga/mixed oxides catalyst was prepared through co-condensation-evaporation method using Ni(NO₃)₂·6H₂O and Ga metal as precursors [33]. Firstly, 2.1g of Ga metal were completely dissolved in 100ml of solution of HNO₃ 2M. The solution was homogeneously mixed with 50ml of solution containing Ni(NO₃)₂. The molar ratio of Ni/Ga was controlled at 5/3. The prepared

solution including metal cations but exceeding acid was neutralised and then precipitated by a suitable concentrated NaOH solution under vigorous stirring until the 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 gel state. The gel was then washed and filtered until the pH of the waste water was neutral. The filtered cakes were dried overnight at 100°C before being introduced to an incinerator at 500°C for 6 hours to obtain Ni-Ga mixed oxide. The mixed oxide was reduced for 5 hours in 100ml of 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.

2.1.3. Preparation of Ni-Ga/mesosilica catalyst

Mesosilica was used as a support for the catalyst, so it should provide high surface area and uniform pore widths. The mesosilica support was prepared by condensation method: in the first step, 150ml of NaOH 0.015M solution was mixed with 2g of CTAB in a round bottle followed by vigorous stirring and slight warming until the CTAB was completely dissolved; the bottle was set up with heating mantle under reflux condition before its temperature was raised to 90°C; 10ml of TEOS was then gradually dropped to the hot bottle while solution's pH was fixed at about 10 by adding dilute NaOH solution; the condensation was established at 90°C for 24 hours; at the end of this step, the solution was kept at this temperature for 2 more hours for settling the precipitate; this precipitate was then decanted before being dried at 110°C overnight. The dried precipitate was then calcined at 550°C for 4 hours under the air for completely burning CTAB from the catalysts structure. The temperature was gradually increased by 2°C per minute. The as-synthesised mesosilica could be used directly for the preparation of the NiGa/mesosilica catalyst.

The NiGa/mesosilica catalyst was prepared by impregnation method using the as-synthesised mesosilica and precursors such as Ni(NO₃)₂ and Ga(NO₃)₃. The impregnation was established step by step through this process: 2g of Ni(NO₃)₂ and Ga(NO₃)₃ calculated from the weights of the hydrate nitrate salts with Ni/Ga molar ratio of 5/3 were instantly dissolved in 30ml of distilled water under light stirring until the solution became homogeneous; then 5g of mesosilica were immersed

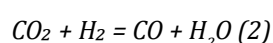
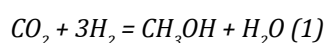
into the solution along with uniformly stirring the mixture; the mixture was then settled in a closed cup for 24 hours under room temperature; an evaporating dish was used for the evaporation of water from the mixture at 120°C for 6 hours; the obtained dried solid was transferred to crucible cup without lid and was introduced to the calcination process at 500°C for 6 hours. After the calcination, the solid was cooled down to room temperature and was filled into NaBH₄ solution in absolute ethanol; the mixture was stirred for around 6 hours at room temperature to carry out the reduction of Ni, Ga cations to alloy state. The catalyst was then also dried at 80°C overnight to obtain the NiGa/mesosilica catalyst. This catalyst could be applied in the conversion of CO₂ to methanol.

2.1.4. Preparation of Ni-Ga-Co/mesosilica

Ni-Ga-Co/mesosilica was prepared in the same way as Ni-Ga/mesosilica through impregnation method. Metal ratio in the catalyst was arranged in a series: Ni/Ga/Co = 5/3/0.1; Ni/Ga/Co = 5/3/0.5 and Ni/Ga/Co = 5/3/1.0.

2.2. Conversion of CO₂ to methanol over catalysts

The process established at a low pressure of 5 bars was conducted on Altamira AMI-902, PVPro, Ho Chi Minh City, Vietnam. Reaction equations in the process could be described as follows:



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 gas phase was fixed at 100ml/min, while the volume of the catalytic bed was 1ml yielding a gas hourly space velocity of 6000h⁻¹. The outlet stream

including many components as unconverted 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 ionisation detector (FID) for analysis of inorganic and organic compounds, respectively. While conversion pressure was fixed at 5 bars, different temperatures were investigated in the range of 150 - 510°C. A 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.

For the high pressure procedure, the process was conducted on Altamira AMI-200, Synchrotron Light Research Institute, Thailand. The conversion of CO₂ to methanol was established with feedstock as a mixture of hydrogen and CO₂ at different H₂/CO₂ volume ratios. Temperature, pressure and H₂/CO₂ volume ratio were investigated in the range of 150 - 350°C; 10 - 50 bars, and 1/1 - 5/1, respectively. Gas sample was collected periodically each 1 hour for the analysis, and 5 to 7 measurements were taken at each collecting time and for calculating the gas composition. The activity and selectivity of CO₂ and methanol were calculated by these compositions. The CO composition was also considered because of its occurrence as a by-product of the process.

2.3. Characterisation

Powder XRD was recorded on a D8 Advance Bruker diffractometer using Cu Kα (λ = 0.15406) radiation. SEM images were captured on Field Emission Scanning Electron Microscope S-4800. TEM images were established on JEM1010-JEOL TEM operated at 80kV. FT-IR analysis was recorded on Nicolet 6700 FT-IR spectrometer. XPS was measured in Kratos Analytical spectrometer fitted with a monochromatic Al X-ray source (1486.7eV). The analysed area was ~ 400 × 400μm². Final

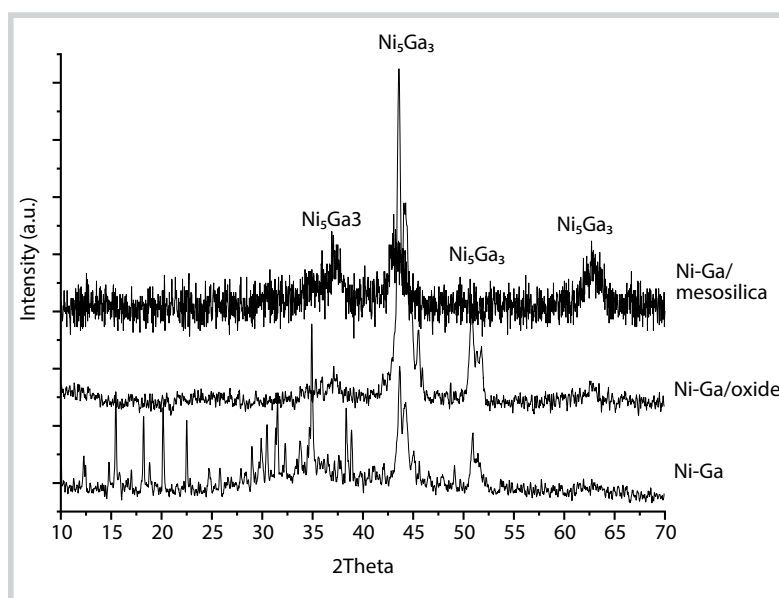


Figure 1. WAXRD patterns of Ni-Ga alloy, Ni-Ga/mixed oxides and Ni-Ga/mesosilica catalysts.

ground powders were pressed into In foil and mounted on an electrically grounded sample holder. The In 3d core level spectrum was measured to be sure that no signal from indium foil was detected. During data processing, the samples were calibrated using C_{1s} line arising from adventitious C with a fixed value of 284.8eV. A Shirley-type function was applied to remove the background arising from energy loss. Gas compositions were determined by GC (Thermo Finnigan Trace GC Ultra) coupled with TCD and FID for determining inorganic and organic compounds, respectively.

3. Results and discussions

3.1. Structure of Ni-Ga alloy, Ni-Ga/mixed oxides and Ni-Ga/mesosilica catalysts

Crystalline properties of the catalysts were characterised 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 besides the desired active phase (Ni₅Ga₃) whose peaks appeared at 2theta ~ 36°, 43°, 50°, 62° [8, 34]. The active sites in the catalyst were mixed with many other components. 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 [8, 35].

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 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 the generation of many by-products besides the desired sites of δ-Ni₅Ga₃; 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 δ-Ni₅Ga₃. 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 δ-Ni₅Ga₃ sites distributed on the mixed oxides of NiO and Ga₂O₃ while the impregnation and reduction of the Ni-Ga/mesosilica mostly produced the δ-Ni₅Ga₃ phase distributed on the amorphous mesoporous silica; the content of the support in the Ni-Ga/mesosilica catalyst which 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 play a crucial role in the distribution of the δ-Ni₅Ga₃ active site over the catalysts surface which would strengthen its stability and activity in the methanol synthesis. Figure 2 plots Small Angle X-Ray Diffraction (SAXRD) patterns of the catalysts and mesosilica support to characterise 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

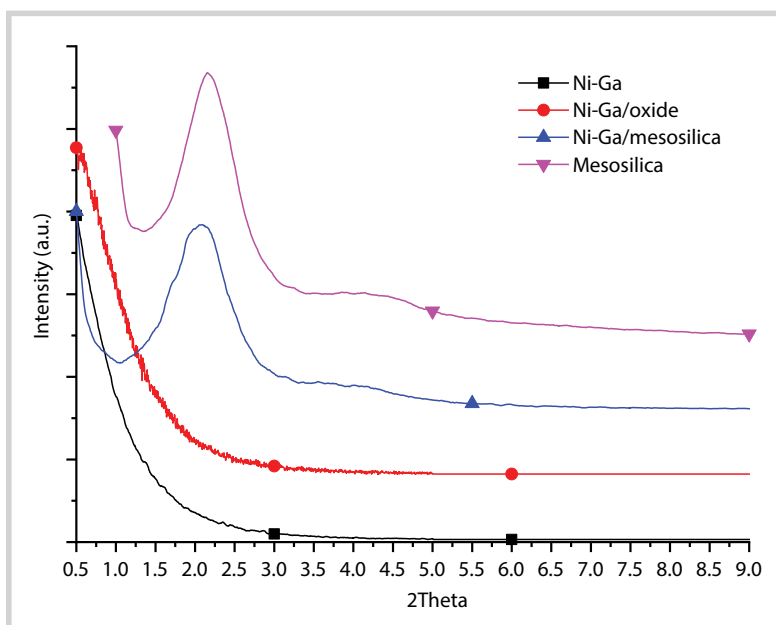


Figure 2. SAXRD patterns of Ni-Ga alloy, Ni-Ga/mixed oxides and Ni-Ga/mesosilica catalysts.

Ni-Ga/mixed oxides, but 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 fingerprint peaks at $2\theta \sim 2^\circ$ and $\sim 4^\circ$ corresponding to (100) and (110) reflection planes in a typical ordered mesoporous material. The intensity of the major peak at $2\theta \sim 2^\circ$ 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 $\delta\text{-Ni}_5\text{Ga}_3$ active site on the surface [36 - 39].

3.2. Morphology of Ni-Ga alloy, Ni-Ga/mixed oxides and Ni-Ga/mesosilica catalysts

Figures 3 and 4 describe 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 uneven sizes attaching together corresponding to poor dispersion of the active sites. The Ni-Ga/mixed oxides catalyst, in contrast, majorly included adjacent spherical-like particles having sizes ranged from 28 - 70nm 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 - 42nm which could be considered as the catalyst with the highest porosity. BET specific surface areas of these Ni-Ga, Ni-Ga/mixed oxides and Ni-Ga/mesosilica catalysts were also adaptable with the predicted porosity results observed in the SEM images: 21.3536m²/g, 137.4325m²/g and 259.0386m²/g, respectively.

TEM images of these catalysts also indicated that the Ni-Ga alloy, Ni-Ga/mixed oxides and Ni-Ga/mesosilica catalysts clearly possessed a dense structure with low porosity, tiny particles inside each large one, and ordered mesoporous channels inside each particle, respectively. The

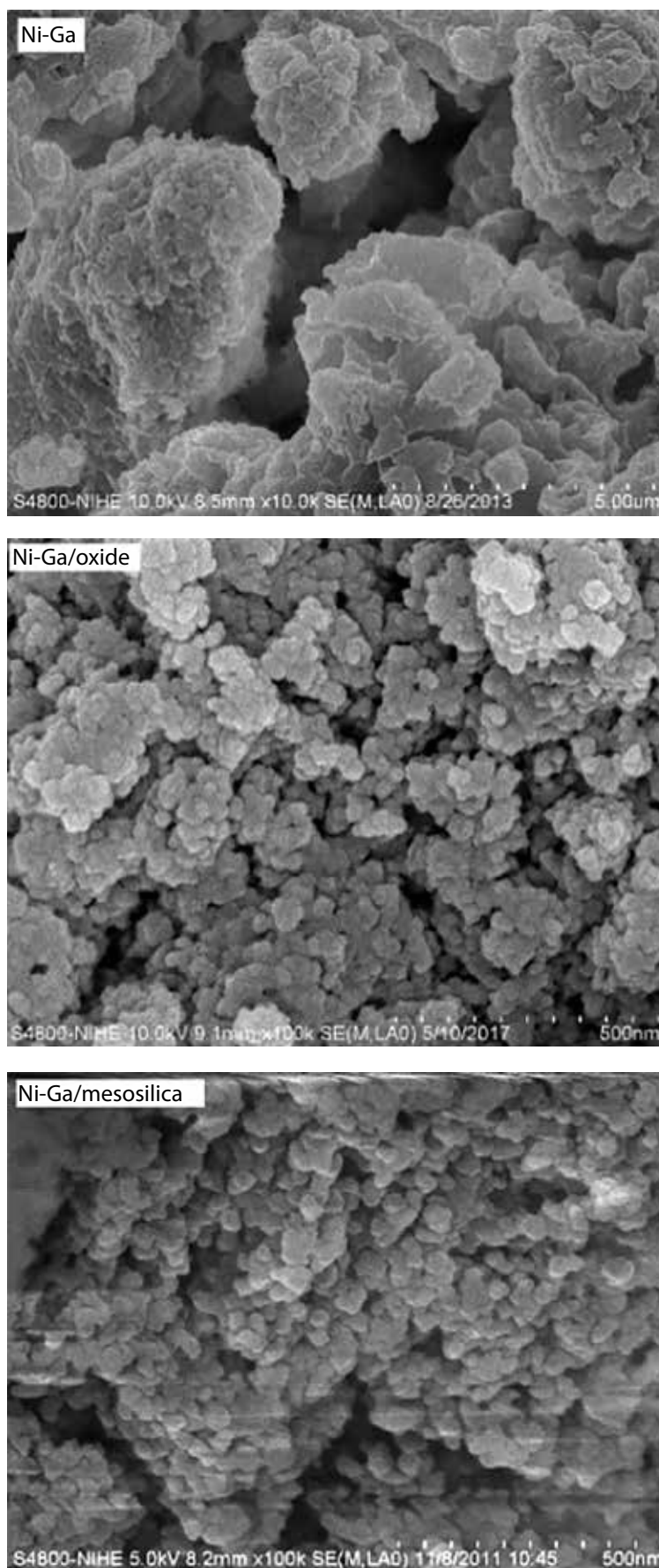


Figure 3. SEM images of Ni-Ga alloy, Ni-Ga/mixed oxides and Ni-Ga/mesosilica catalysts.

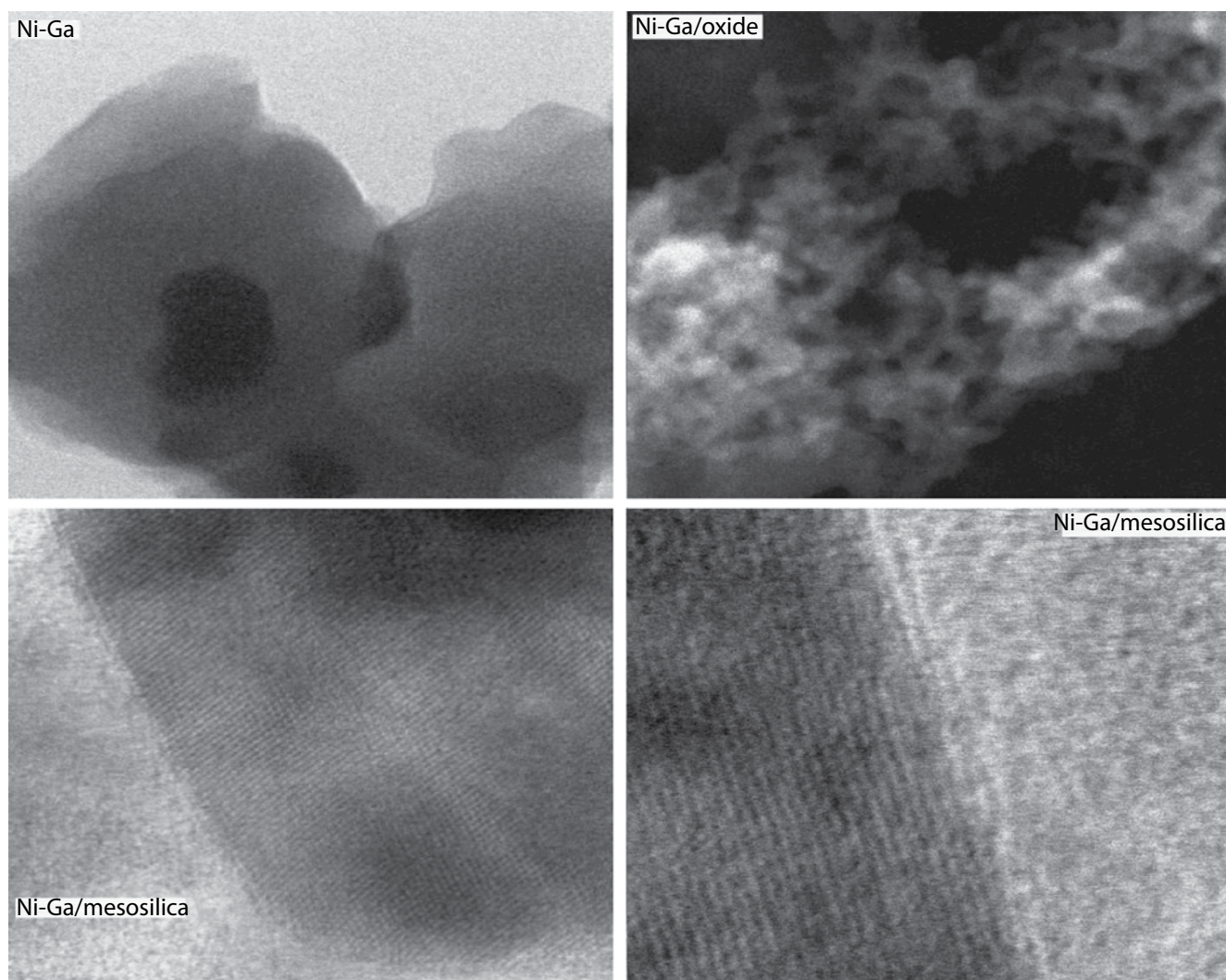


Figure 4. TEM images of Ni-Ga alloy, Ni-Ga/mixed oxides and Ni-Ga/mesosilica catalysts.

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 also be easily understandable when considering the different preparation methods of these catalysts. There were some important points which could also be noted when inspecting the properties of these catalysts through their structure and morphology characterisations: the Ni-Ga alloy catalyst had the highest crystallinity but the lowest content of the $\delta\text{-Ni}_5\text{Ga}_3$ active site caused by the metal melting preparation; the Ni-Ga/mixed oxides catalyst had good purity of the $\delta\text{-Ni}_5\text{Ga}_3$ active sites, good crystallinity but not possessed an ordered mesoporous system; the Ni-Ga/mesosilica had high purity of the $\delta\text{-Ni}_5\text{Ga}_3$ 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 $\delta\text{-Ni}_5\text{Ga}_3$ active sites. As a consequence, the Ni-Ga/mesosilica catalyst was chosen for its potential of having high activity in the methanol synthesis. XPS analysis was established with this catalyst to illustrate its chemical element states.

3.3. Conversion of CO_2 to methanol over Ni-Ga alloy, Ni-Ga/mixed oxides and Ni-Ga/mesosilica catalysts at low pressure condition

The investigation was established by fixing the reaction pressure at 5 bars, H_2/CO_2 volume ratio of 3/1. Table 1 - 3 collected results obtained from each catalysis testing process due to temperature rising.

The results obtained from these analyses over the three catalysts pointed out that CO_2 was converted to other forms such as CO , CH_4 and C , in which CO and C were the main products. There were many biases relating to the C content in the product because of its complicated forms

Table 1. Product composition varied by temperature for the process over Ni-Ga alloy catalyst at low pressure.

T (°C)	H ₂	CO ₂	CO	CH ₄	C	CH ₃ OH
150	75.14	26.15	0	0	0	0
180	74.95	25.14	0	0	-0.26769	0
210	75.89	26.2	0	0	0.191205	0
240	75.25	25.98	0	0	-0.6501	0
270	75.08	26.05	0	0	-0.38241	0
300	75.12	25.85	0.03	0	-1.0325	0
330	74.83	25.66	0.14	0	-1.33843	0
360	75.66	25.33	0.34	0	-1.83556	0
390	74.45	23.86	0.7	0.02	-6.00382	0
420	74.32	23.14	1.31	0.04	-6.34799	0
450	74.02	22.63	2.15	0.15	-4.66539	0
480	72.94	17.88	5.88	0.36	-7.76291	0
510	71.43	15.64	7.83	1.7	-3.74761	0

Table 2. Product composition varied by temperature for the process over Ni-Ga/mixed oxides catalyst at low pressure.

T (°C)	H ₂	CO ₂	CO	CH ₄	C	CH ₃ OH
150	75.05	24.89	0	0	0	0
180	74.95	25.14	0	0	-0.83532	0
210	75.04	24.89	0	0	-0.83532	0
240	75.18	25.08	0	0	-0.23866	0
270	75.2	25.04	0	0	-0.7955	0
300	75.13	24.8	0.04	0	-1.19332	0
330	75.3	24.5	0.16	0	-1.90931	0
360	75.48	24.1	0.4	0	-2.54574	0
390	75.51	23.44	0.85	0.04	-3.22196	0
420	74.4	21.66	2.35	0.41	-2.86396	0
450	70.1	18.45	4.33	1.79	-2.2673	0
480	69.58	17.42	5.44	3.9	6.443914	0
510	63.84	16.33	5.32	9.97	25.77566	0

Table 3. Product composition varied by temperature for the process over Ni-Ga/mesosilica catalyst at low pressure.

T (°C)	H ₂	CO ₂	CO	CH ₄	C	CH ₃ OH
100	75.26	22.16	0	0	0	0
150	75.14	22.02	0	0	-0.63177	0
180	74.96	22.05	0	0	-0.49639	0
210	74.87	22.23	0	0	0.315884	0
240	75.02	22.09	0	0	-0.31588	0
270	75.14	22.04	0	0.008	-0.54152	0
300	75.14	21.94	0	0.011	-0.99278	0
330	75.06	21.71	0.38	0.011	-0.31588	0
360	73.97	21.13	0.79	0.015	-1.08303	0
390	74.04	20.38	1.73	0.07	-0.22563	0
420	73.65	19.35	2.9	0.086	0.406137	0
450	73.41	18.54	4.28	0.08	2.978339	0
480	72.79	16.86	5.67	0.09	1.669675	0
510	72.15	15.86	7.54	0.12	5.595668	0
515	72.52	14.87	8.32	0	4.648014	0
520	72.17	14.91	8.59	0	6.046931	0

in the reaction media making it difficult to precisely measure its composition. However, the generation of carbon is a negative effect on the catalyst lifespan.

There was no evidence of generated methanol. The reason for that was that the CO₂ conversion to methanol was a volume decrease reaction. Therefore, thermodynamically, a high pressure condition was required to accelerate the conversion in the direction of producing methanol. The tests of the process at high pressure were conducted in Thailand.

3.4. Conversion of CO₂ to methanol over Ni-Ga alloy, Ni-Ga/mixed oxides and Ni-Ga/mesosilica catalysts at high pressure condition

3.4.1. Screening of catalyst

The screening process was implemented over three prepared catalysts including Ni-Ga alloy, Ni-Ga/mixed oxides and Ni-Ga/mesosilica. The process pressure and temperature were fixed at 35 bars and 220°C, respectively. Because the most important component of the product was methanol, the catalysis performance was based on two factors: conversion of CO₂ and selection of methanol. Figure 5 plots the main investigation of catalytic activity based on the selection of methanol. The investigations were conducted over the three catalysts.

The obtained results showed that the process conducted over the Ni-Ga/mesosilica exhibited the highest value of methanol selections which was suitable with the catalysis characterisation on its structure and active site distribution (XRD, SEM and TEM). The plotted curve describing the selection of methanol over the Ni-Ga/mesosilica catalyst also revealed the lowest changes corresponding to the good catalysis stability during the process. Contrastingly, the methanol selection for the process over Ni-Ga alloy catalyst was the lowest value, and the catalyst activity did not last for long because of its low stability. The Ni-Ga/mixed oxides performance was

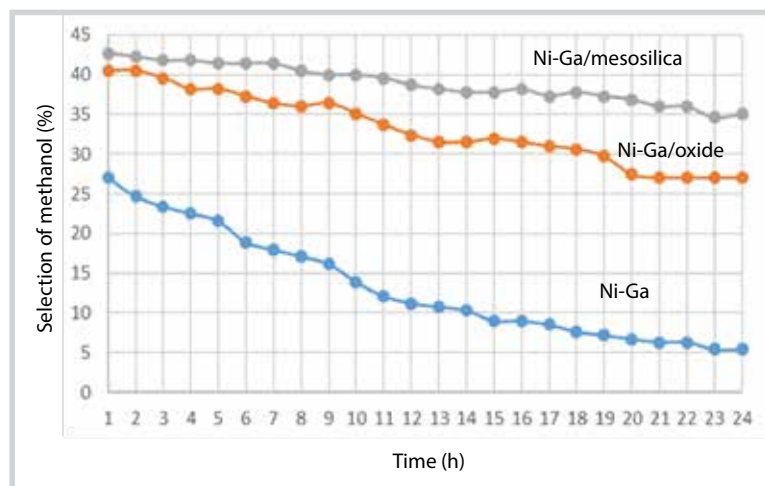


Figure 5. Methanol selection over Ni-Ga alloy, Ni-Ga/mixed oxides and Ni-Ga/mesosilica catalysts.

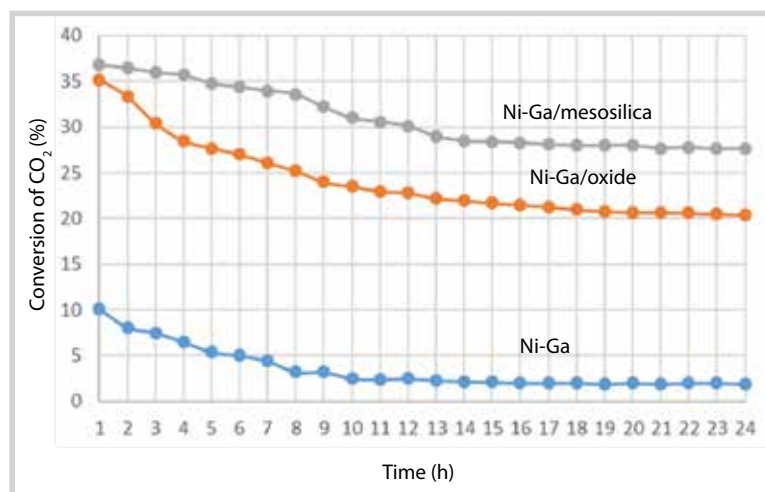


Figure 6. CO2 conversion over Ni-Ga alloy, Ni-Ga/mixed oxides and Ni-Ga/mesosilica catalysts.

Table 4. Effect of temperature on gas composition in products.

T (°C)	H ₂ (%)	CO ₂ (%)	CO (%)	CH ₄ (%)	CH ₃ OH (%)
100	72.26	22.73	1.01	0.00	2.11
150	70.14	20.01	2.02	0.00	3.14
180	68.36	19.14	2.98	0.00	5.20
210	64.35	17.98	3.26	0.00	6.37
240	60.82	16.83	4.78	0.00	7.29
270	56.99	15.58	5.12	0.00	8.59
300	56.33	14.21	5.96	0.00	8.03
330	55.48	13.38	6.38	0.00	7.88
360	54.23	12.24	7.45	0.00	7.13
390	52.93	11.38	8.93	0.00	6.54
420	52.01	11.35	9.31	0.00	6.00
450	50.99	10.56	10.33	0.00	5.39
480	49.68	10.01	11.67	0.00	4.12
510	49.02	9.43	12.01	0.00	3.22
510	48.61	8.72	12.75	0.00	1.94
510	47.86	8.02	13.05	0.00	1.51

laid on the intermediate between the Ni-Ga alloy and Ni-Ga/mesosilica catalysts. On the other hand, the CO₂ conversions of the process over these catalysts were also investigated and plotted in Figure 6.

The obtained results exhibited a common trend among these catalysts: the CO₂ conversion would be gradually reduced to a constant value after a certain period of time. With the Ni-Ga/mesosilica and Ni-Ga/mixed oxide catalysts, the CO₂ conversion was high at the beginning (36.8% and 35.2%), then decreased to a constant value after 16 hours of contact; the Ni-Ga alloy catalyst showed the lowest performance when the beginning conversion of CO₂ reached only 10.1%, then stabilised at 2% after 10 hours of contact. That was to say, the Ni-Ga/mesosilica catalyst exhibited the highest performance among these three. The reason for these results could be assigned to two factors:

- Firstly, the nature and composition of Ni-Ga based catalysts: according to the authors [1, 2], Ni₅Ga₃ active site at high temperature possessed the characteristics of n type semiconductor yielding to the continuous movement of intrinsic free electrons and empty positive holes. This would increase the decomposition of adsorbed hydrogen from the H₂ to H form over Ni sites. This led to an increase in the catalytic activity in the conversion of CO₂. Otherwise, the Ni-Ga sites could play an important role in the adsorption of CO for weakening the C=O p bonding connections inside the molecule leading to the acceleration of the CO₂ reduction to methanol.

- Secondly, the effect of supports: the catalysis performances could be arranged by the list of Ni-Ga/mesosilica > Ni-Ga/mixed oxide > Ni-Ga alloy, suitable with the order of site distribution over the supports. Possessing the Ni₅Ga₃ sites well distributed on the mesoporous silica support, the Ni-Ga/mesosilica would be the best candidate in this aspect. Therefore, the Ni-Ga/mesosilica catalyst was chosen for the further investigation of the CO₂ conversion in various parameters.

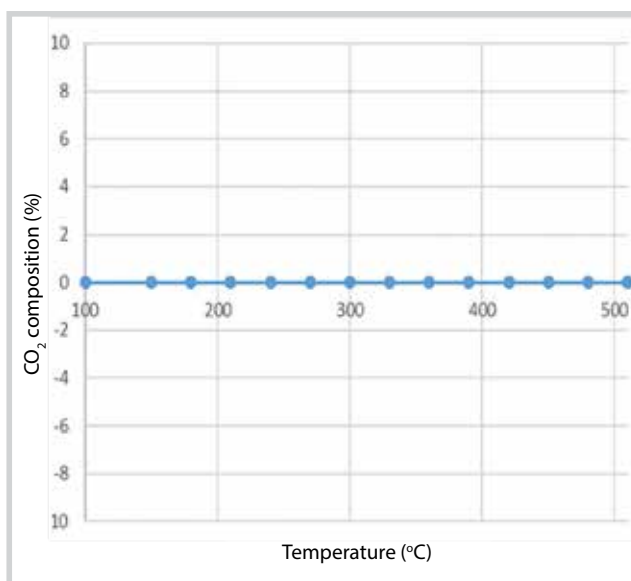
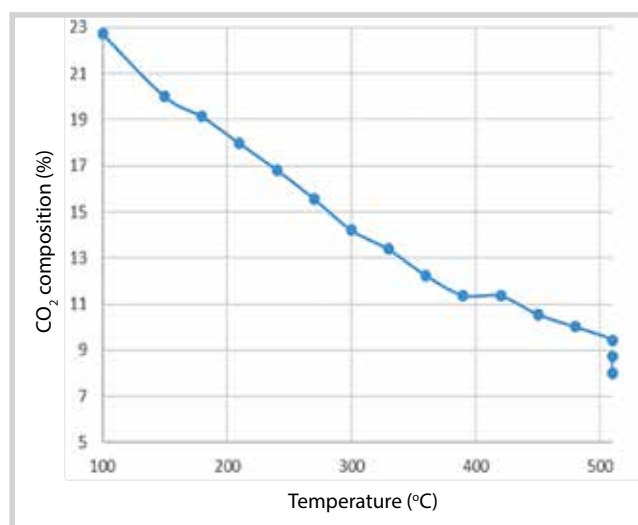
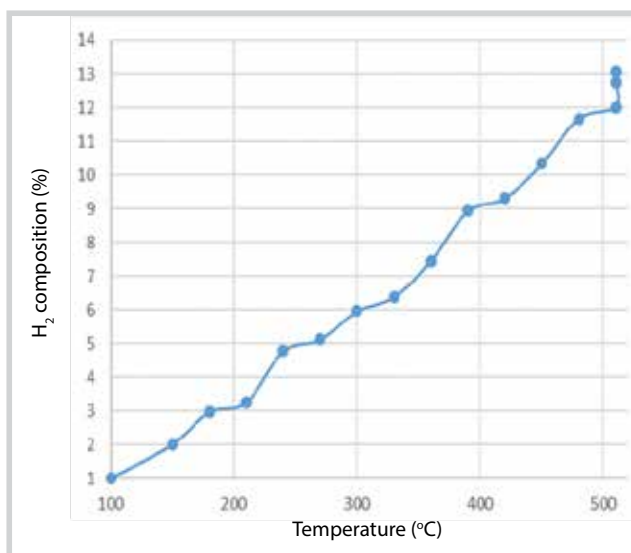
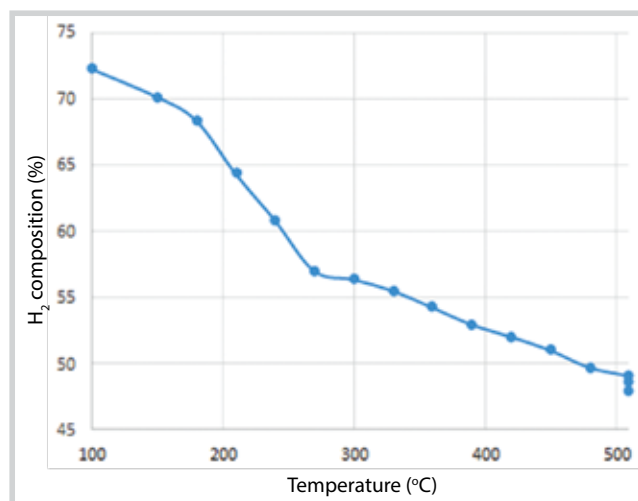


Figure 7. Effect of temperature on H₂ and CO₂ composition.

3.4.2. Investigation of CO₂ conversion over Ni-Ga/mesosilica catalyst

There were many factors affecting the conversion of CO₂ to methanol such as temperature, pressure, H₂/CO₂ volume ratio, and time of the reaction. The investigations were based on two main target factors: conversion of CO₂ and selection of methanol. These factors could be calculated from the gas composition of the end products.

a. Effect of temperature

Temperature played a very important role in the conversion. The investigation was established by fixing the reaction pressure at 35 bars, H₂/CO₂ volume ratio of 3/1. Table 4 and Figures 7 and 8 collect and plot the results.

Results clearly indicated common trends in the gas composition due to the reaction's temperature: increasing

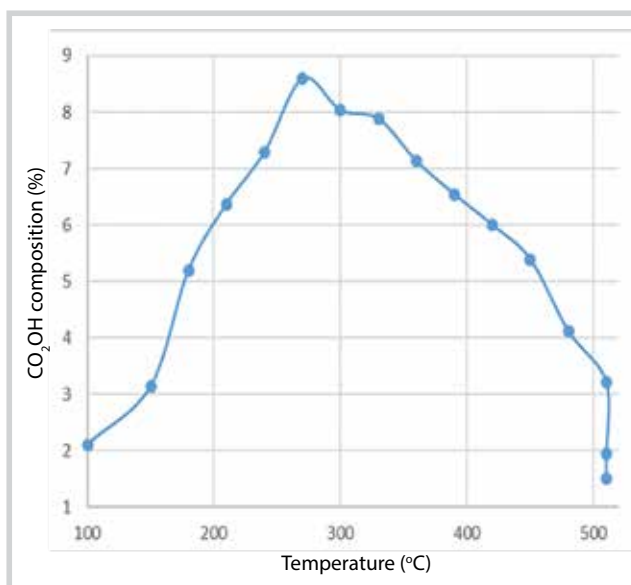


Figure 8. Effect of temperature on CO, CH₄ and CH₃OH composition.

Table 5. Effect of pressure on gas composition in products.

P (bar)	H ₂ (%)	CO ₂ (%)	CO (%)	CH ₄ (%)	CH ₃ OH (%)
10	70.94	22.46	4.80	0.00	3.80
15	68.41	21.02	4.87	0.00	4.11
20	66.96	20.23	4.90	0.00	5.65
25	62.23	17.94	4.93	0.00	6.95
30	58.26	16.22	4.99	0.00	7.86
35	57.01	15.55	5.11	0.00	8.60
40	56.98	15.51	5.11	0.00	8.61
45	56.90	15.22	5.13	0.00	8.61
50	56.88	15.00	5.11	0.00	8.62

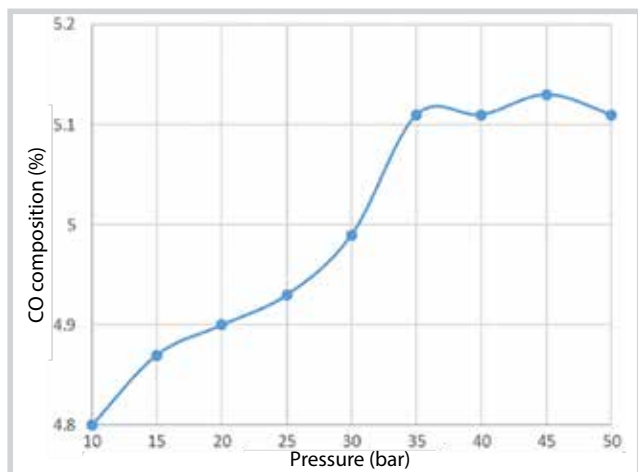
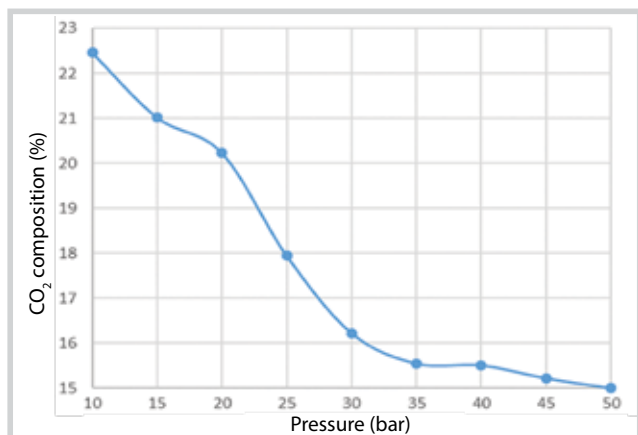
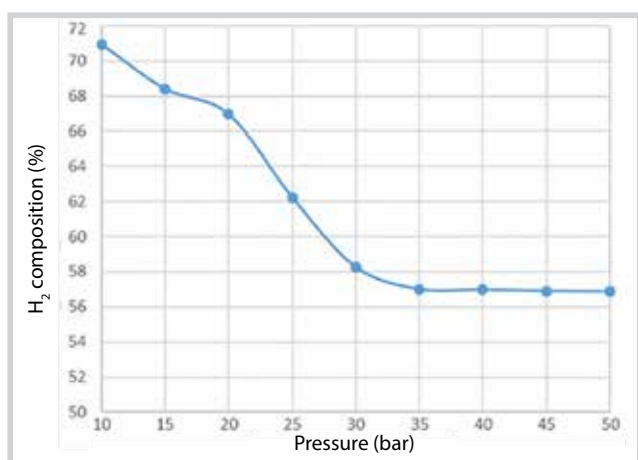


Figure 9. Effect of pressure on H₂, CO₂ and CO composition.

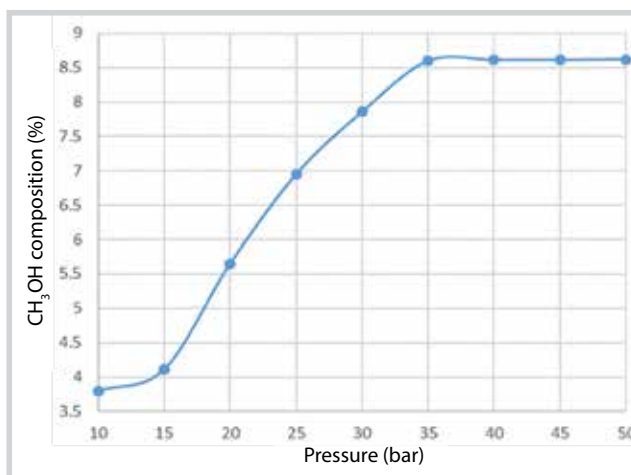
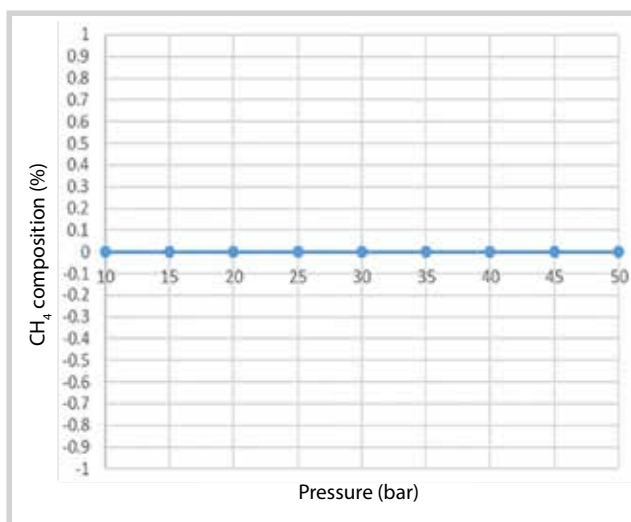


Figure 10. Effect of pressure on CH₄ and CH₃OH composition.

Table 6. Effect of H₂/CO₂ volume ratio on gas composition in products.

H ₂ /CO ₂	Conversion of CO ₂ (%)	Selectivity of CH ₃ OH (%)
1/1	30.22	58.50
1.5/1	35.35	60.45
2/1	38.68	61.81
2.5/1	41.28	62.36
3/1	46.62	62.68
3.5/1	46.83	62.05
4/1	47.12	61.37
4.5/1	47.21	60.98
5/1	47.35	60.12

the temperature led to decreasing the compositions of H₂ and CO₂ in outlet streaming corresponding to their higher conversion at higher temperatures; however, the composition of CO increased by increasing the temperature while the generation of CH₄ was still very restricted; the composition of methanol varied at different temperature and peaked at 270°C; at higher temperature, the selectivity for methanol decreased.

It could be said that the process established at 35 bars became much more effective than being established at atmospheric pressure. It could also be based on the thermodynamic of such reactions for a reasonable explanation: because the reaction (1) was volume-decreased and exothermic, it could be favourable for implementing the process at high pressure and high enough temperature; the investigation showed that the best temperature for this process was 270°C; the reaction (2) was slightly endothermic and constant volume, so increasing the temperature led to slightly increasing the selectivity of CO; the reaction (3) was also volume-decreased, but it could not compete with the two previous reactions. On the whole, the temperature of 270°C was favourable for the investigation, in which the methanol content reached 8.59% by volume, and the CO, CH₄ generations were limited well; especially, no carbon formation was a good behaviour because it could well improve the catalyst's stability.

b. Effect of pressure

The pressure of the process changed from 10 bars to 50 bars while other parameters were kept such as the temperature of 270°C, H₂/CO₂ volume ratio of 3/1. Results of the process were collected and plotted in Table 5 and Figures 9 and 10.

The profile relating to the effect of pressure on such process was different from the effect of temperature: the composition of CO₂ and H₂ decreased by the increase of pressure from 10 bars to 35 bars and became stable after that; the CO composition slowly increased and also became constant after reaching 35 bars, and there was still no trace of CH₄ in the outlet gas components; unlike CO₂ and H₂, the methanol composition gradually increased by the increase of pressure from 10 bars to 35 bars and also was constant at higher pressure.

Explanations for these results were also rooted in the thermodynamic properties of the reaction (1) and (2) which were volume-decreased and constant volume, respectively. Equation (1) would shift in the direction of producing more products, so the methanol content was high. However, the methanol composition would be stable at a high enough pressure because the restriction of the reaction's temperature was 270°C. Equation (2) was not affected by varying the pressure because of its constant volume property, but the composition of CO was still of slight increase due to the decrease of the volume of

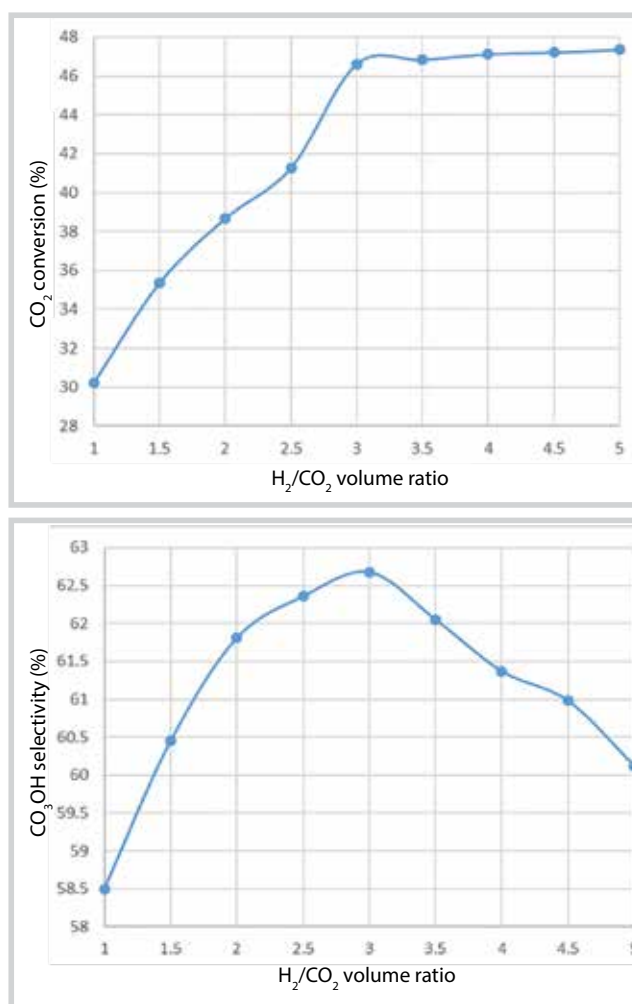


Figure 11. Effect of H₂/CO₂ volume ratio on CO₂ conversion and methanol selectivity.

the feedstock and the whole process. The pressure of 35 bars was suitable for the process.

c. Effect of H₂/CO₂ volume ratio

The stoichiometry of the equation (1) was H₂:CO₂ = 3:1, so the investigations of the H₂/CO₂ volume ratio would vary around that value. These were 0.5/1; 1/1; 1.5/1; 2/1; 2.5/1; 3/1; 3.5/1; 4/1; 4.5/1; 5/1, being established during the fixing of other parameters such as temperature and pressure at 270°C and 35 bars, respectively. Because of the changes in feedstock composition, the outlet gas composition would not precisely reflect the variations of CO₂ conversion as well as CH₃OH selectivity. In this case, the CO₂ conversion and CH₃OH selectivity could be considered as the main factors for the investigation. In fact, calculation could be easily made to determine the CO₂ conversion and methanol selection from the gas composition. The results of the investigation were collected in Table 6 and plotted in Figure 11.

Table 7. Effect of time on gas composition in products.

Time (h)	Conversion of CO ₂ (%)	Selectivity of CH ₃ OH (%)
1	46.9	62.7
2	46.5	62.3
3	46.1	61.8
4	45.6	61.8
5	44.9	61.6
6	44.5	61.6
7	44.1	61.6
8	43.7	60.5
9	42	60
10	41	60
11	40.6	59.6
12	40.1	58.7
13	39	58.2
14	38.5	57.8
15	38.4	57.8
16	38.3	58.2
17	38.1	57.5
18	38	57.8
19	38	57.5
20	38	56.9
21	37.7	56
22	37.8	56
23	37.6	54.6
24	37.7	54.3
25	37.6	54.3
26	37.5	54.2
27	37.5	54.2
28	37.4	54.1
29	37.4	54
30	37.4	54
31	37.2	54
32	37.3	53.9
33	37	54
34	37	53.9
35	36.7	53.8
36	36.5	53.5
37	36.4	53
38	36.3	52.7
39	36.2	52.5
40	36	52.1
41	35.7	51.6
42	35.5	51.4
43	35.2	51.4
44	34.4	50.2
45	34	49.1
46	33.2	48.7
47	32.5	47
48	31.4	46.5
49	30.1	45
50	28.7	43.4
51	27.8	41.8
52	25.8	39.5
53	23.1	38.2
54	20.2	37.1
55	18.9	36.9
56	17.6	36.3
57	15.1	36
58	12.2	35.4
59	10	33.4
60	10	34.2

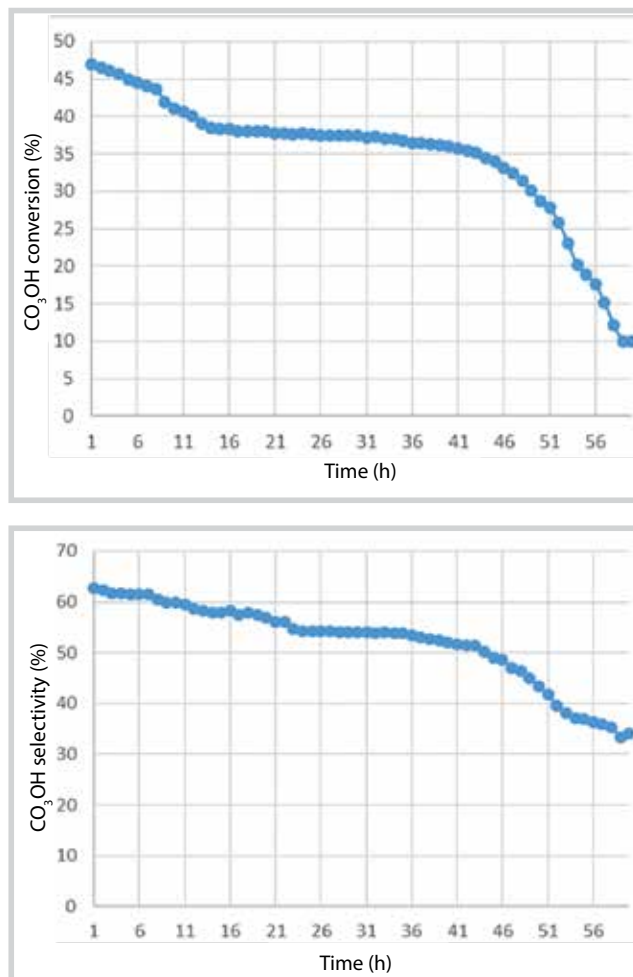


Figure 12. Effect of reaction time on CO₂ conversion and methanol selectivity.

The investigations showed that increasing the H₂/CO₂ volume ratio could raise the CO₂ conversion to a high and stable value. In contrast, the profile of the CH₃OH selectivity could reach a peak at the ratio of 3/1. These were also caused by the thermodynamic characteristics of the equations (1) and (2). When the volume ratio was high, there was an excess of H₂ in the process yielding the shift of equations (1) and (2) into the direction of increasing the CO₂ conversion. However, the conversion could only reach the highest value of 47%. The selectivity of CH₃OH also accelerated when the volume ratio of H₂/CO₂ was up to 3/1; then it would reduce when this ratio was higher than 3/1. This was caused by the competition of the side reactions (2) producing a larger amount of CO at the high volume ratios of H₂/CO₂. Hence, the H₂/CO₂ volume ratio applied for the process should be 3/1 for enhancing both the CO₂ conversion and the CH₃OH selectivity. These values achieved 62.68% for the former and 46.62% for the later parameters meaning the CH₃OH yield of the whole process of 29.22%. Compared to many

other studies [4, 8, 13 - 16], the CH₃OH yield was much higher demonstrating the good activity of the NiGa/mesosilica catalyst.

d. Effect of contacting time

There was a big difference between the process established by the batch reactor and the process carried out by the continuous reactor. In the batch reactor, the process was completed after an exact

period of time before the whole products were analysed for their chemical compositions. In contrast, the continuous process included reaction and analysis at the same time. Therefore, the investigation of time for the continuous process played in both

Table 8. Samples of Ni-Ga-Co/mesosilica catalyst

No.	Sign	Metal molar ratio
1	M1	Ni/Ga/Co = 5/3/0.1
2	M2	Ni/Ga/Co = 5/3/0.5
3	M3	Ni/Ga/Co = 5/3/1.0

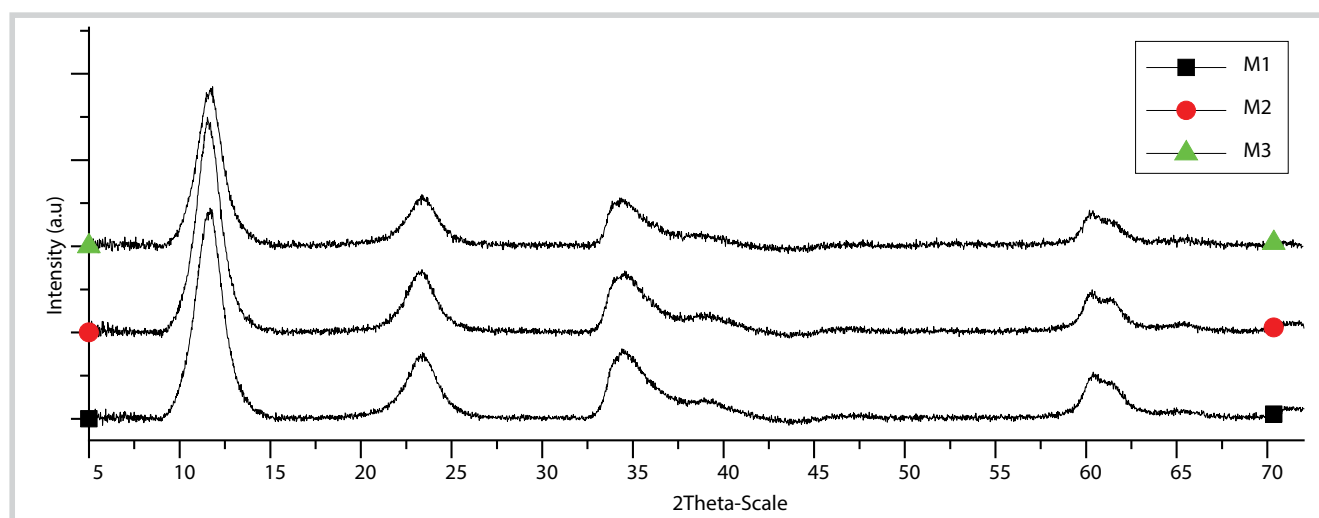


Figure 13. WAXRD patterns of Ni-Ga-Co/mesosilica catalysts before reduction.

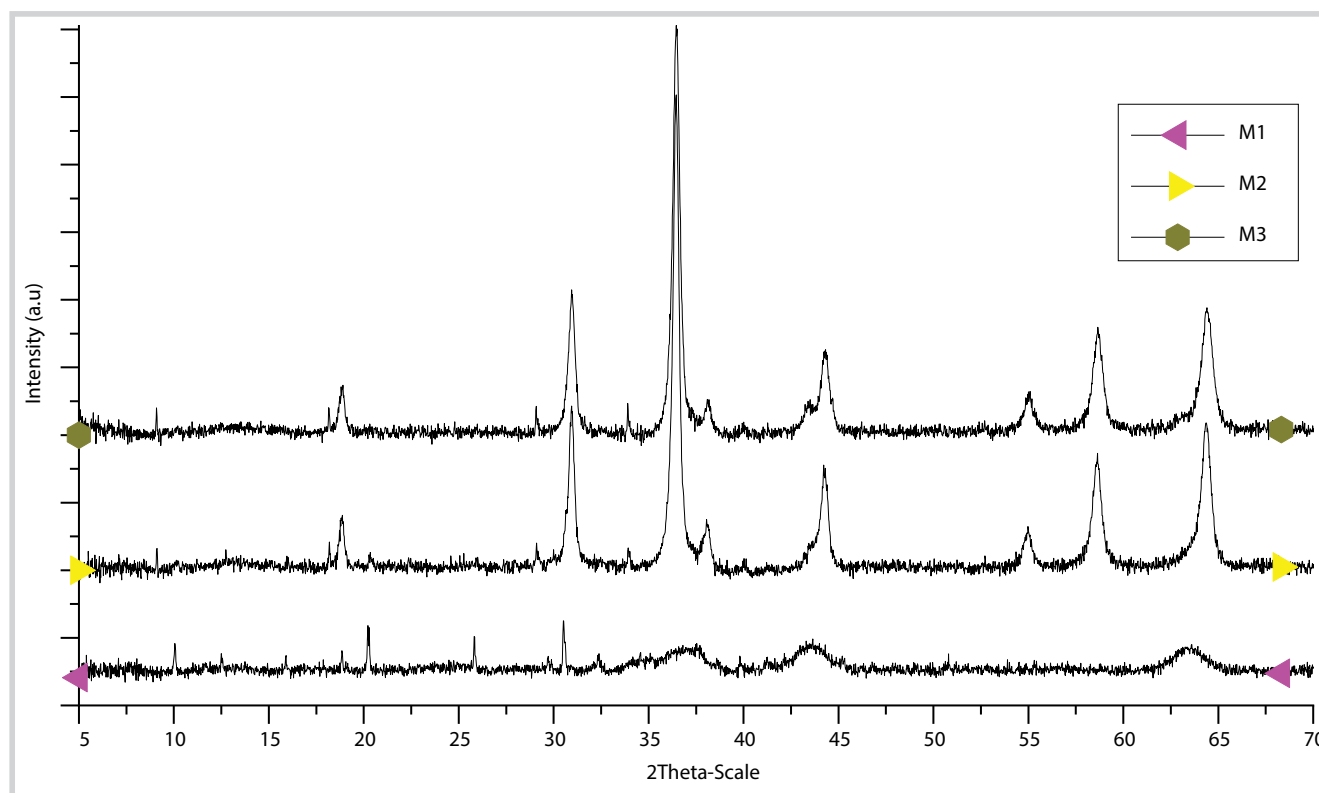


Figure 14. WAXRD patterns of Ni-Ga-Co/mesosilica catalysts after reduction.

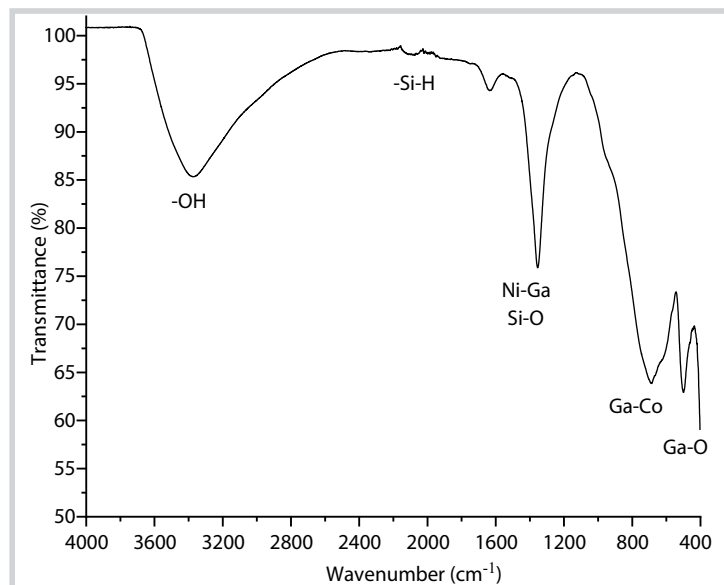


Figure 15. FT-IR spectra of M2 catalyst.

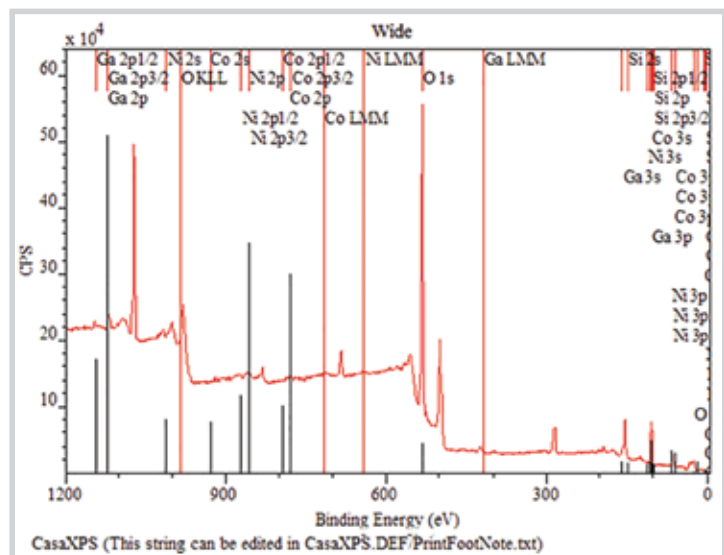


Figure 16. XPS spectra of M2 catalyst.

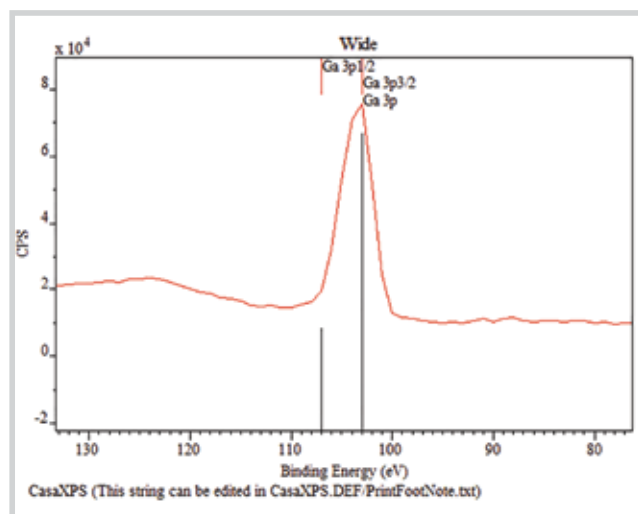


Figure 17. XPS spectra of Ga site in M2 catalyst.

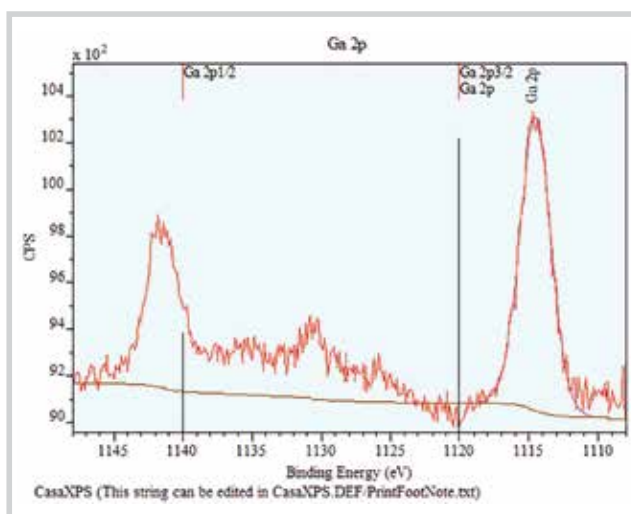
roles: estimation of the reaction performance, and consideration of the catalyst stability (or the catalyst life span). In this investigation, the results collected and analysed in Table 7 and Figure 12 could be applied for both purposes.

The results obtained from the investigations indicated that the conversion of CO₂ and the selectivity of CH₃OH could both maintain their stability until 45 hours of the process reflected by the slight decreases in such values. After 45 hours, the catalyst became less active corresponding to the sharp decreases in both the conversion and selectivity of the related molecules. On the whole, the total investigations exhibited a set of suitable parameters for the process such as temperature of 270°C, time of 45 hours, pressure of 35 bars and H₂/CO₂ volume ratio of 3/1. In such conditions, the conversion of CO₂ and selectivity of CH₃OH were 46.9% and 62.7%, respectively. The yield of the whole process was 29.4%.

3.5. Characterisation of Ni-Ga-Co/mesosilica catalyst

For the improvement of the Ni-Ga/mesosilica activity, another metal component as a promoter was introduced to the catalyst. The Co promoter was chosen because Co²⁺ had the same cation dimension with Ni²⁺. The Ni-Ga-Co/mesosilica catalysts with different metal molar ratios were prepared and assigned in Table 8.

The WAXRD patterns of the Ni-Ga-Co/mesosilica catalysts before reduction plotted in



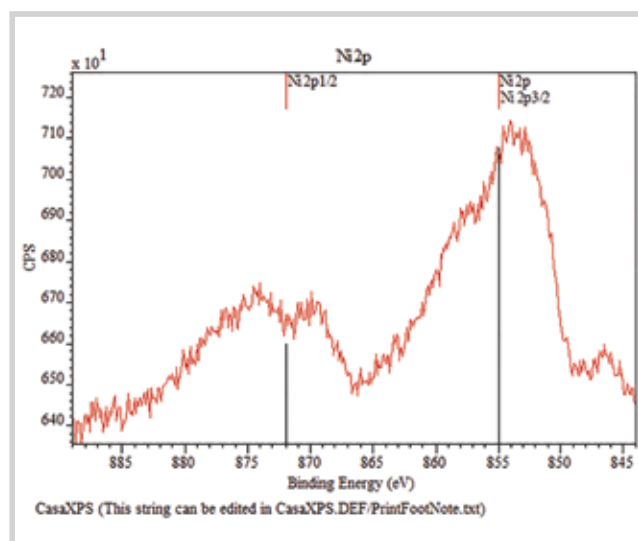


Figure 18. XPS spectra of Ni site in M2 catalyst.

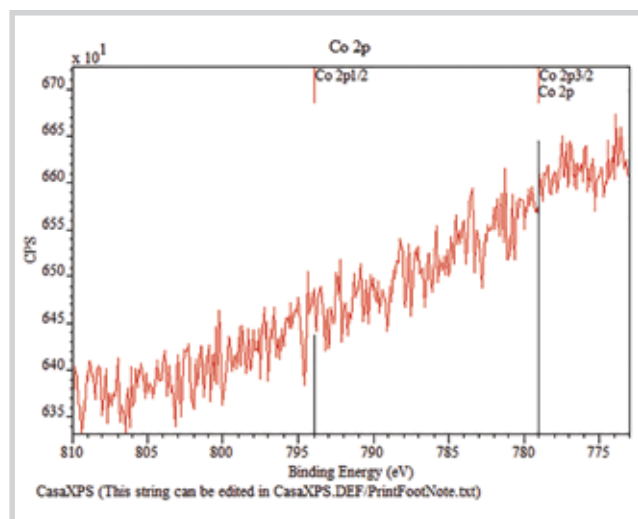
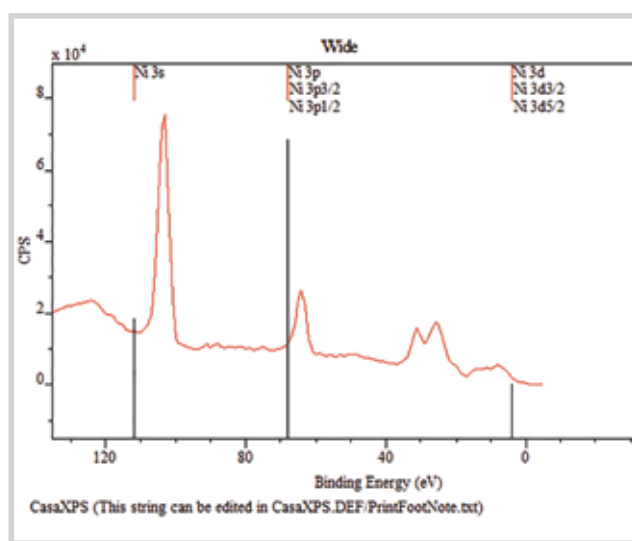


Figure 19. XPS spectra of Co site in M2 catalyst.

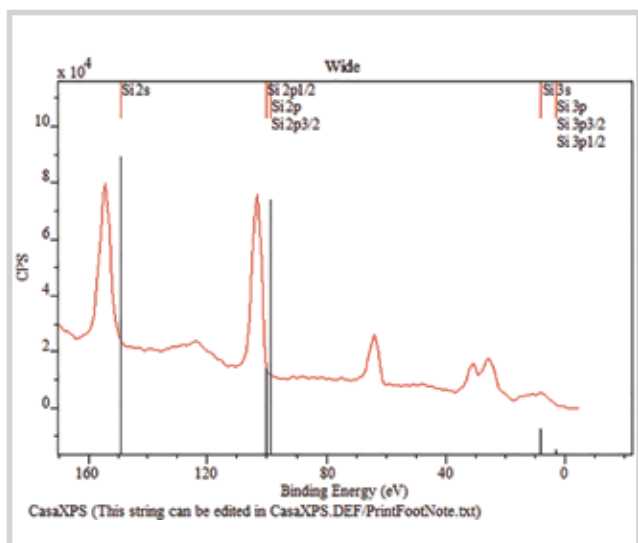
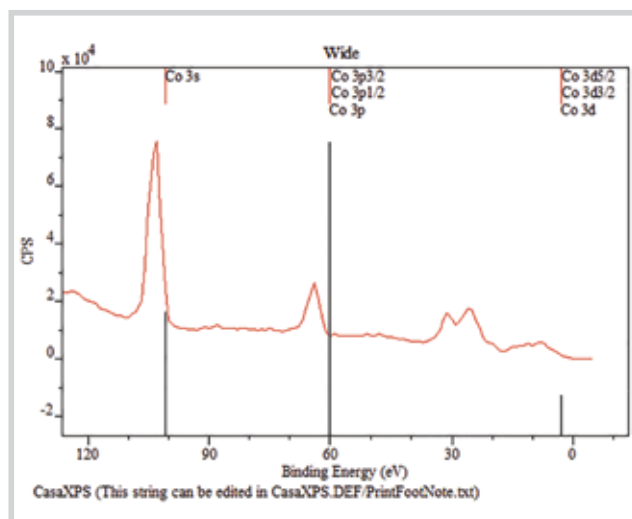


Figure 20. XPS spectra of Si site in M2 catalyst.

Figure 13 clearly showed the stable structure of the Ni-Ga-Co/mesosilica catalysts before being reduced under hydrogen. These were all in hydroxalcite-like structure with $2\theta = 11.8^\circ, 23.4^\circ, 34.5^\circ$ and 60.7° . That clarified an isomorphic substitution of Co^{2+} into the framework of Ni-Ga hydroxalcite like compound.

The WAXRD patterns of the Ni-Ga-Co/mesosilica catalysts after reduction plotted in Figure 14 exhibited Ga-Co crystal at $2\theta = 31.2^\circ$ and 54.9° , Ga_2O_3 crystal at $2\theta = 18.7^\circ$ and 36.7° , besides the Ni_5Ga_3 active site at $2\theta = 43.8^\circ, 57.5^\circ$ and 64.2° . The introduction of Co to the Ni-Ga framework was purposed to stabilise the active sites of Ni_5Ga_3 under the high temperature of the reaction. Moreover, the Ni site would be more flexible and reactive with adsorption of surface hydrogen; then the catalyst

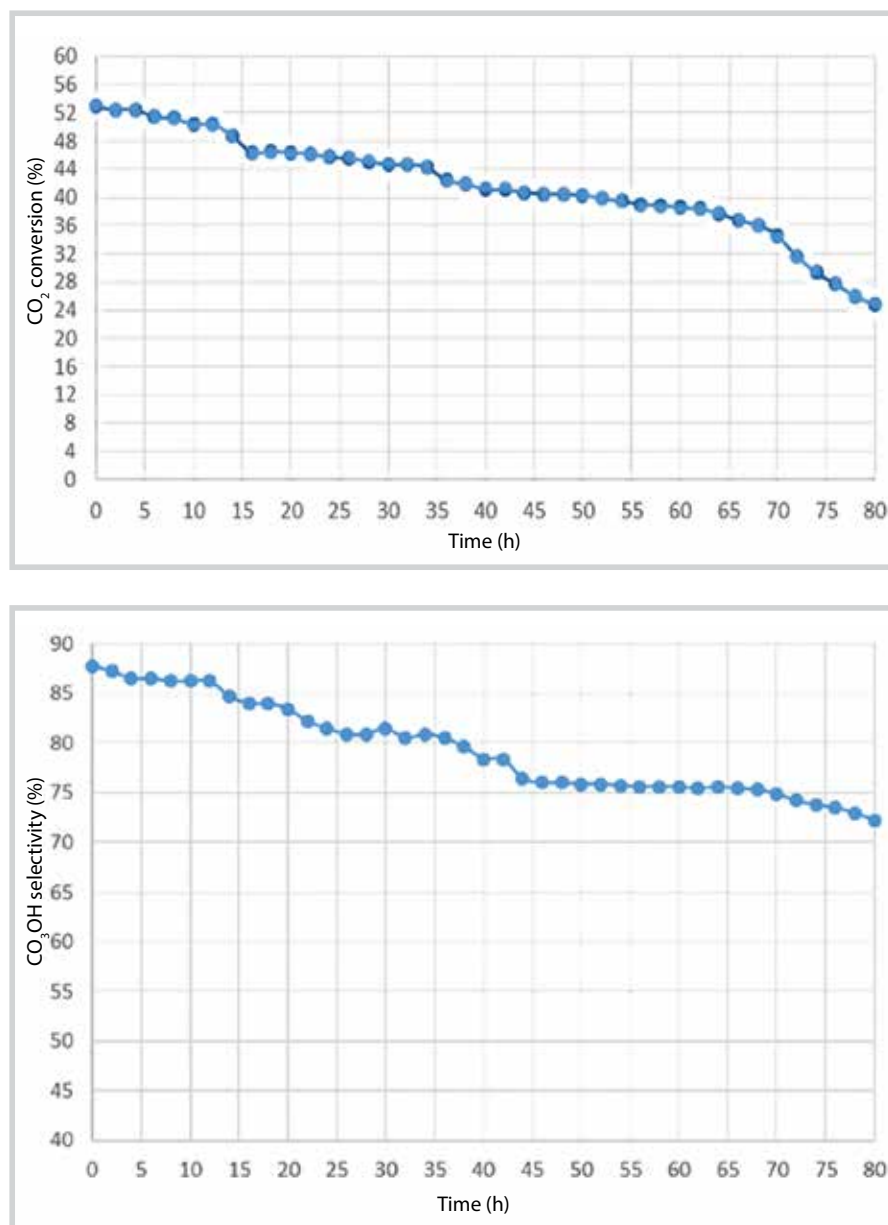


Figure 21. CO₂ conversion and methanol selection at pressure of 35 bars.

activity could be raised at lower pressure [8, 11]. Because the crystallinity of the M2 sample was the highest, it was chosen for further characterisation and application.

The FT-IR spectra of the M2 catalyst indicated specialised peaks for meso-SiO₂ support and Ni-Ga-Co based alloys at the wavenumbers of ~3400cm⁻¹, 2050cm⁻¹, 1400cm⁻¹, 700cm⁻¹ and 500cm⁻¹, as mentioned in Figure 15. The FT-IR spectra confirmed the appearance of the bonding connection between alloy phases in the metals and the support.

XPS spectra in total and partial ranges were plotted in Figures 16 - 20. Results demonstrated that the Ga signals in the M2 catalyst were metal and oxide states at bond energies of 1115eV and 103.1eV, respectively. However, the content of Ga in oxide state was very low illustrating that the reduction in NaBH₄/ethanol solution was highly effective in transforming Ga³⁺ to Ga⁰ [8].

XPS spectra for Ni sites showed that Ni metal existed at bond energy of 870eV, 853eV and 64eV. There was no trace for Ni in oxide state (112eV), so the whole Ni²⁺ was reduced to Ni⁰ after treatment with NaBH₄ solution. There were energy shifts at both high and low energy regions corresponding to Ni occurred in the alloy instead of the separated metal state. Also, there was evidence of energy shift characterised for the Ni connected with the mesosilica support [8].

XPS spectra of Co site also showed no peak in 770-810eV assigned for CoO (Cobalt II oxide) demonstrating that the Co²⁺ was totally reduced to Co metal. The alloyed metal state of Co was exhibited at bond energies of 103eV and 65eV.

XPS spectra of Si site sharply indicated signal of silica SiO₂ at bond energies of 103eV and 155eV. There was an energy shift to the higher value compared to normal silica [8, 40] proving that there were contacts between the support and the alloyed metal state of these metals. The contacts between the support and the alloyed metal strongly enhanced the distribution of the active site and stabilised it under the process conditions.

3.6. Activity of Ni-Ga/mesosilica and Ni-Ga-Co/mesosilica in conversion of CO₂ to methanol

For the activity comparison, the conversion of CO₂ to methanol process was established in both low and high pressure conditions.

3.6.1. Conversion of CO₂ to methanol over Ni-Ga/mesosilica catalyst

On the whole, as mentioned

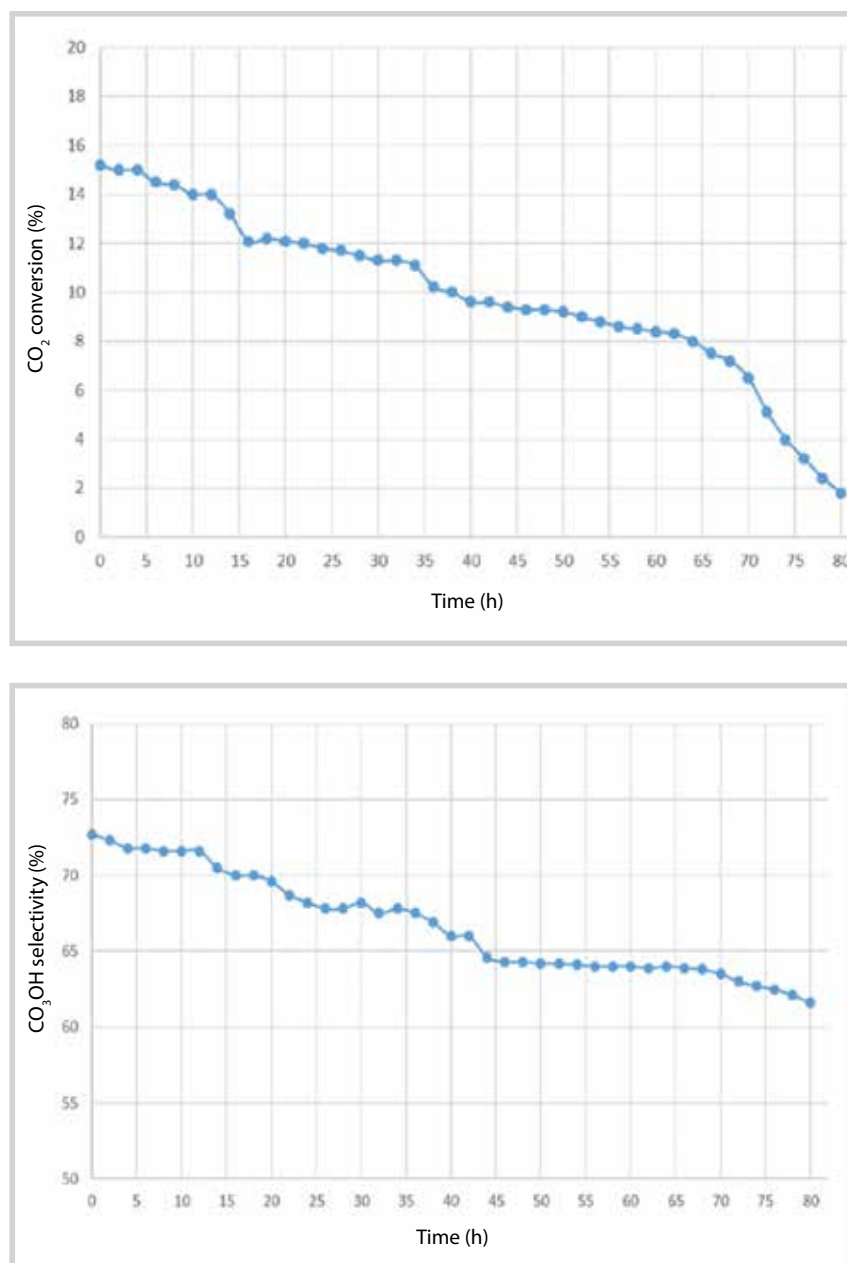


Figure 22. CO₂ conversion and methanol selection at pressure of 5 bars.

previously, the total investigations exhibited a set of suitable parameters for the process such as temperature of 270°C, time of 45 hours, pressure of 35 bars and H₂/CO₂ volume ratio of 3/1. In such conditions, the conversion of CO₂ and the selectivity of CH₃OH were 46.9% and 62.7%, respectively. The yield of the whole process was 29.4%.

3.6.2. Conversion of CO₂ to methanol over Ni-Ga-Co/mesosilica catalyst

Investigations were conducted by the same steps as being conducted over the Ni-Ga/mesosilica. Results obtained from the process established at 35 bars and 5 bars were plotted in Figures 21 and 22, respectively.

Results exhibited that the CO₂ conversions for the processes over the

Ni-Ga-Co/mesosilica and Ni-Ga/mesosilica were 52.0% and 46.9% respectively, which pointed out that there was an increase in the CO₂ conversion after modifying the catalyst. Results exhibited that the methanol selections for the processes over the Ni-Ga-Co/mesosilica and Ni-Ga/mesosilica were 85.0% and 62.7% respectively, which strongly confirmed that the methanol selection was much improved after modifying the catalyst. It could be said that, at the high pressure of 35 bars, the performance of the Ni-Ga-Co/mesosilica was higher than that of the Ni-Ga/mesosilica catalyst.

In low pressure of 5 bars, although the conversion of CO₂ sharply decreased compared to the case of 35 bars, the methanol selectivity of methanol was still high and much higher than the case using the Ni-Ga/mesosilica catalyst. That strongly demonstrated the introduction of Co into the Ni-Ga/mesosilica catalyst clearly enhanced the catalytic performance in the conversion of CO₂ to methanol process. On the whole, the process conducted over the Ni-Ga-Co/mesosilica catalyst achieved some major results: pressure of 35 bars, temperature of 270°C, CO₂ conversion of 52%, methanol selection of 85%, catalysis life-span of 70 hours.

4. Conclusion

- Preparation and characterisation of Ni-Ga alloy, Ni-Ga/mixed oxides, Ni-Ga/mesosilica and Ni-Ga-Co/mesosilica catalysts were conducted using the metallic melting, co-condensation-evaporation and impregnation methods. In which, the Ni-Ga alloy possessed the highest crystallinity, the lowest purity and the lowest porosity; the Ni-Ga/mixed

oxides contained high purity Ni₅Ga₃ crystals distributed on NiO-Ga₂O₃ mixed oxides; the Ni-Ga/mesoporous silica and Ni-Ga-Co/mesoporous silica also contained high purity Ni₅Ga₃ crystals distributed over mesoporous amorphous silica, and these two catalysts possessed the best texture property for stabilising the Ni₅Ga₃ active site.

- Investigation of CO₂ conversion under hydrogen at the low pressure of 5 bars over the Ni-Ga alloy, Ni-Ga/mixed oxides and Ni-Ga/mesoporous silica catalysts indicated that there were no generation of methanol but many other by-products such as CH₄, Co and C. The investigation at the high pressure of 35 bars pointed out that the best candidate for the process was the Ni-Ga/mesoporous silica catalyst, under the following conditions and results: pressure of 35 bar, temperature of 270°C, catalysis life-span of 45 hours, H₂/CO₂ volume ratio of 3/1, CO₂ conversion of 46.9%, methanol selection of 62.7 %, and the total yield of the process reaching 29.4%.

- Activity of the Ni-Ga-Co/mesoporous silica in both low and high pressure was much better than that of the Ni-Ga/mesoporous silica proving that the introduction of Co into the Ni-Ga/mesoporous silica greatly enhanced its catalytic property and stability. The results obtained from the process are as follows: pressure of 35 bars, temperature of 270°C, CO₂ conversion of 52%, methanol selection of 85% and catalysis life-span of 70 hours.

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