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Study on preparation of ordered mesoporous silica supported NiGaCo catalyst for conversion of carbon dioxide to methanol

Hong Khanh Dieu Nguyen[1] · **Nguyen Ngoc Tran**[1] · **Ngo Thi Dinh**[1] · **Toan Dang Nguyen**[1] · **Don Ngoc Ta**[2] · **Duc Sy Dao**[3]

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Abstract

The paper reported preparation, characterization and application of novel ordered mesoporous silica supported NiGaCo catalyst in direct conversion of carbon dioxide to methanol. The catalyst was prepared by doping Ni^{2+}, Ga^{3+} and Co^{2+} onto ordered mesoporous amorphous silica support (MSO) through wet impregnation–condensation method followed by calcination and reduction to transfer the metallic cation states to the alloy ones. The catalyst was assigned as NiGaCo/MSO, being prepared under conditions such as room temperature, time of 24 h, calcination at 600 °C for 6 h, and reduction in $NaBH_4$/ethanol solution, and could be used for converting CO_2 to methanol at low pressure. Investigations illustrated high activity of the catalyst at high pressure of 35 bars but at low pressure of 5 bar, the catalyst still showed considerable activity and selectivity. Many techniques were applied for the catalysis characterization including Small Angle X-Ray Diffraction (SAXRD), Wide Angle X-Ray Diffraction (WAXRD), Fourier Transform-Infrared Spectroscopy (FT-IR), Thermal Gravimetric–Differential Scanning Calorimetry–Mass Spectroscopy (TG–DSC–MS) and X-Ray Photoelectron Spectroscopy (XPS). Gas Chromatography (GC) coupled Thermal Conductivity Detector (TCD) and Flame Ionized Detector (FID) were used for determining the gas composition.

Keywords Mesoporous silica · Ni_5Ga_3 · Methanol synthesis · Carbon dioxide · Cobalt promoter

1 Introduction

Methanol could be considered as a fuel, precursor or energy storage source in industrial economy because of its easy storage and transportation. Using methanol in industrial chemistry processes has been estimated a crucial development nowadays. Some of aspects when using methanol could be described as followed: high octane rate (107–115), high effectiveness in fuel cell, excellent candidate for dimethyl ether production, high cetane number (55) also, an important source for olefin production and then the most chemicals in cosmetic and industrial substances. Methanol economy once was mentioned because of these advanced properties [1–4].

Methanol could be synthesized from syn-gas (CO and H_2 mixture at certain ratio) using many types of catalysis, for example ZnO supported Cu [5, 6], mixed ZnO and Al_2O_3 supported Cu [6, 7], mixed ZnO, Al_2O_3 and ZrO_2 supported Cu [7], and Pd based catalysts as well [8–11], etc. The drawbacks of these catalysts were pointed out in either low activity, selectivity or high expense. The synthesis of methanol over these catalysts could require parameters such as 50–100 bars, high temperature, but in this conditions, competition of CO formations was considerable. Therefore, many aspects of them need to be enhanced and controlled, especially the high pressure applied in each process [12–16]. The recent development has opened a new candidate as the Ni–Ga alloy catalyst, which provided a greener method for consuming many sources of greenhouse CO_2 and produced one of the most useful beginning chemical in chemistry industry. Some researches said that they belonged to one of the most active and effective catalysts for this kind of direct conversion, especially the active site of the catalysts was Ni_5Ga_3 alloy [8, 9]. According to the reports [12, 13], performance of the Ni–Ga alloy applied in the CO_2 conversion could surpass most existed supported metal catalysts. However, they also

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✉ Hong Khanh Dieu Nguyen
hong.nguyenkhanhdieu@hust.edu.vn

[1] Hanoi University of Science and Technology, Hanoi, Vietnam

[2] Ministry of Education and Training, Hanoi, Vietnam

[3] VNU University of Science, Hanoi, Vietnam

confirmed that the selectivity of methanol could be further improved at lower pressure of H_2 and CO_2.

From our approaching, effectiveness of the Ni–Ga based catalyst could be strongly improved by enhancing its active site (Ni_5Ga_3) distribution over various types of support. The support possessed higher specific surface area than the alloy one, and it could help to strengthen the active site distribution. The Ni–Ga/mesosilica reported in another paper [17], behaved as the best candidate for the conversion of CO_2 to methanol at mild pressure (30–35 bar). However, the pressure of the process was not mild enough and need to be further reduced.

An important realization 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 Ni_5Ga_3 active sites under the process conditions. Therefore, improving the active site distribution by using a good support was not enough to stabilize the catalysis effectiveness. In this case, metal promoter could be considered as an important factor for overcoming the drawbacks. Further studies led to preparation of NiGaCo/MSO (as mentioned—MSO: ordered mesoporous amorphous silica support) catalyst where Co as a promoter 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 Ni_5Ga_3 active sites during the conversion.

2 Experimental

2.1 Chemicals

Chemicals with analytical pure (> 99%) were used including $Ni(NO_3)_2{\cdot}6H_2O$, $Ga(NO_3)_3{\cdot}9H_2O$, $Co(CH_3COO)_2$, NaOH, Na_2CO_3, $NaBH_4$, TEOS (Tetraethyl Orthosilicate), C_2H_5OH and CTAB (Cetyltrimethylammonium Bromide), from Merck, Germany. Distilled water was prepared at local lab. Feedstock such as hydrogen and CO_2 gases were domestically ordered.

2.2 Preparation of NiGaCo/MSO catalyst

2.2.1 Preparation of ordered mesoporous amorphous silica (MSO)

The MSO support was prepared by condensation method including these following steps:

Firstly, 150 ml of NaOH 0.015M solution was homogeneously mixed with 2 g of CTAB in a round bottle coupled with heating mantle, reflux equipment and thermometer. The temperature of the mixture was then risen to 90°C under stirring by turning the heat and stir function of the heating mantle.

Secondly, TEOS was carefully and gradually drop-wise to the bottle while fixing the solution's pH at about 10 by adding the dilute NaOH solution. The condensation process was established at 90 °C for 24 h. The mixture was then settled and cooled for 2 h followed by separating the precipitate. The precipitate was filtered, washed by the deionized water, and dried at 110 °C for 24 h.

Thirdly, the dried precipitate was gradually heated to 550°C and last for 4 hours under the air. In this process, the CTAB template was completely burned leaving the mesoporous hole channels.

2.2.2 Preparation of NiGaCo/MSO catalyst

The NiGaCo/MSO catalyst was prepared by impregnation–condensation method using the as-synthesized MSO and precursors such as $Ni(NO_3)_2$, $Ga(NO_3)_3$ and $Co(CH_3COO)_2$. The process was established as described: 3 g of $Ni(NO_3)_2$, $Ga(NO_3)_3$ and $Co(CH_3COO)_2$ with different Ni/Ga/Co molar ratios (fixing Ni/Ga molar ratio of 5/3, the 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) were completely dissolved in 30 ml of the deionized water under stirring; then 7.5 g MSO was mixed into the solution.

10 ml of Na_2CO_3 solution 10% was then added to the mixture under stirring vigorously. The stirring was continued for 24 h at room temperature. The mixture was then transferred to an evaporating dish for evaporation of water at 120 °C for 3 h. The dried solid obtained after that was transferred to a crucible cup without lid and was introduced to a calcination process at 600 °C for 6 h.

After the calcination, the solid was cooled down to room temperature and was filled into 100 ml of $NaBH_4/C_2H_5OH$ solution. The mixture was stirred for around 6 hours more at room temperature to carry out the reduction of the metal cations to the alloy states. The solid after filtering was then dried at 80 °C overnight to obtain the NiGaCo/MSO catalyst.

2.3 Conversion of CO_2 to methanol over NiGaCo/MSO catalyst

The process established at a low pressure of 5 bars and a high pressure of 35 bar. They were all conducted on Altamira AMI-200, Synchrotron Light Research Institute, Thailand. Reaction equations in the process could be described as follows:

$$CO_2 + 3H_2 = CH_3OH + H_2O \quad (1)$$

$$CO_2 + H_2 = CO + H_2O \quad (2)$$

Firstly, the catalyst was re-activated at 220 °C for 3 h under hydrogen flow of 30 ml/min. Secondly, the process was established under these conditions: H_2/CO_2 volume ratio of 3/1, total gas flow of 100 ml/min, gas hourly space velocity of 6000/h. The outlet was analyzed by GC-TCD and GC-FID machines (Thermo Finnigan Trace GC Ultra).

The pressure of the process was fixed at 5 bars while the temperature was kept at 270 °C. Gas sampling was implemented each 1 h, and the measurement was carried out through 5 to 7 times. Based on the analyzed gas compositions, the conversion of CO_2, the selection of methanol, and the total yield of the process could be clearly calculated.

2.4 Characterization

Techniques including XRD, FT-IR, TG–DSC–MS, XPS and GC were measured on a D8 Advance Bruker, Nicolet 6700 FT-IR spectrometer, Metler Toledo TGA/DSC 2 Star* supported MS detector of ThermoStar™, Kratos Analytical spectrometer and Thermo Finnigan Trace GC Ultra coupled with TCD and FID for, respectively.

3 Results and discussions

3.1 Structure of MSO support

Ordered mesoporous structure of the MSO support was demonstrated by SAXRD method plotted in Fig. 1. Observations from the pattern clearly showed the peaks at $2\theta \sim 2.2°$ and $2\theta \sim 4.2°$ corresponding to (100) and (110) diffraction planes, respectively, specified for the ordered mesoporous structure [18–20]. These peaks were also familiar with the ones observed from the SAXRD patterns of other typical mesoporous materials such as MCM-41 [21, 22]. On the other hand, strong intensity of the (100) peak and clear distinguish of the (110) peak were a good evident corresponding to the high degree of order of the mesoporous channels in the support. This brought the MSO support with great texture characteristics for loading and diffusing many types of active sites such as acid, base, metals, oxides, etc.

The amorphous structure of the MSO support was also exhibited in WAXRD method (Fig. 2). The background removal WAXRD pattern plotted in Fig. 2 clearly showed only SiO_2 signal between 2θ of 20° and 30° which was very similar to amorphous silica structure [18–20]. There was also no signal of crystals illustrating that the mesoporous wall was built from the silica units.

The amorphous structure provided an important characteristic for the formation of the ordered mesoporous structure as it was isotropic [21, 22].

3.2 Characterizations of NiGaCo/MSO catalyst

As a development of the NiGa/MSO catalyst [17, 23], another metal component as a promoter was introduced to the catalyst. The Co promoter was chosen because Co^{2+} had the same cation dimension with Ni^{2+}, and in many situation, had been used as a promoter for Ni based catalysts [24]. The NiGaCo/MSO catalysts with different metal molar ratios were prepared and assigned in Table 1, and their WAXRD patterns were plotted in Fig. 3.

The WAXRD patterns of the NiGaCo/MSO catalysts before reduction plotted in Fig. 3 clearly showed their similar and stable structure before being reduced under hydrogen atmosphere. These were all in double layered structure with 2theta = 11.8°, 23.4°, 34.5° and 60.7° [25]. The result

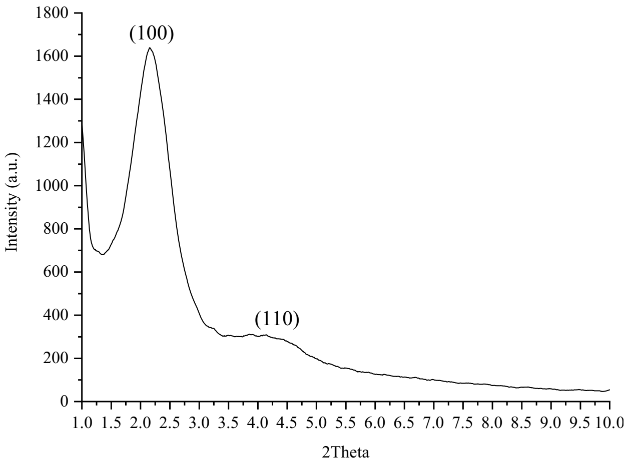

Fig. 1 SAXRD patterns of MSO

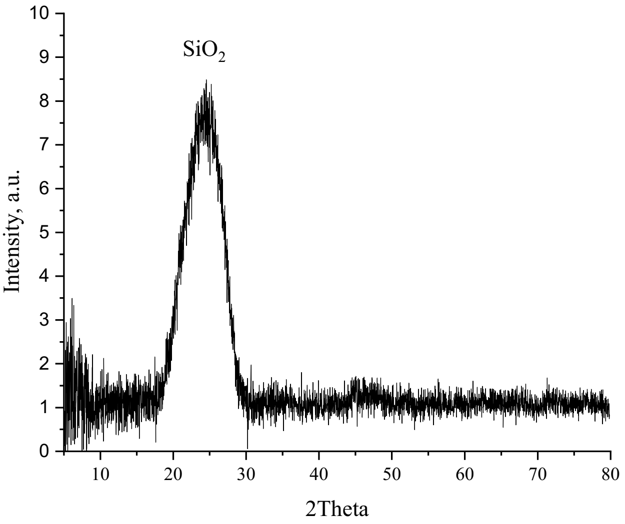

Fig. 2 WAXRD patterns of MSO

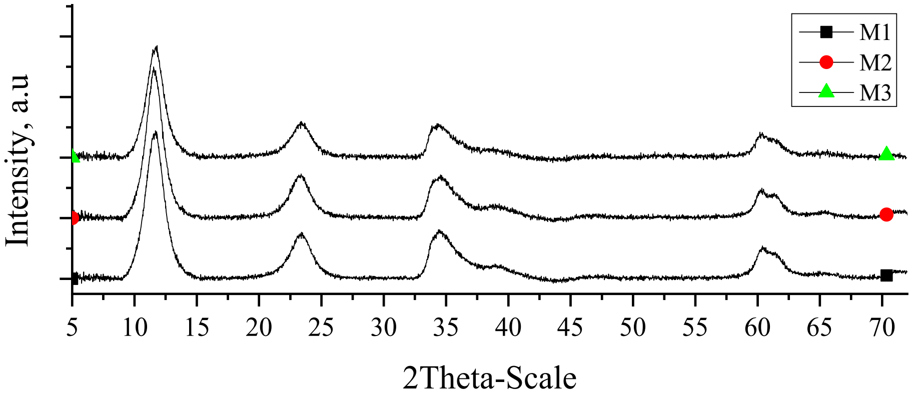

Fig. 3 WAXRD patterns of NiGaCo/MSO catalysts before reduction

Table 1 Samples of NiGaCo/MSO 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

also confirmed an isomorphic substitution of Co^{2+} into the framework of the original NiGa double layered structure.

The WAXRD patterns of the NiGaCo/MSO catalysts after calcination and reduction plotted in Fig. 4 exhibited Ga–Co crystal phase at $2\theta = 31.2°$ and $54.9°$, Ga_2O_3 crystal at $2\theta = 18.7°$ and $36.7°$, besides the Ni_5Ga_3 active site at $2\theta = 43.8°$, $57.5°$ and $64.2°$ [12, 13, 25]. The introduction of Co to the NiGa 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. They were all effective in raising the catalyst activity at lower pressure compared to the other types of catalysts [12].

The ordered mesoporous structure of these catalysts was also demonstrated by SAXRD method. The SAXRD patterns of them were plotted in Fig. 5.

The results observed from the Fig. 5 clearly revealed the good stability of the ordered mesoporous structure of the MSO support which keeping its fingerprint peaks at (100) planes through all the catalysis samples [21, 22]. There were some shifts in the peak position and decrease in peak intensity when raising the Co content corresponding to expanding of the pore width and to lowering of the degree of order. It was an obvious observation compared to many other supported mesoporous materials including MCM and SBA types as introduced metals could affect the mesopores by many ways, for example, by opening the pore holes because of their large particle size, leading to decrease the order of the silica wall in the materials. However, the most important property of the catalyst was to keep the mesoporous structure and diffusing the Ni_5Ga_3 active sites over the support; then by this purpose, these catalysts could be good candidates for the conversion of CO_2 to methanol. Because the

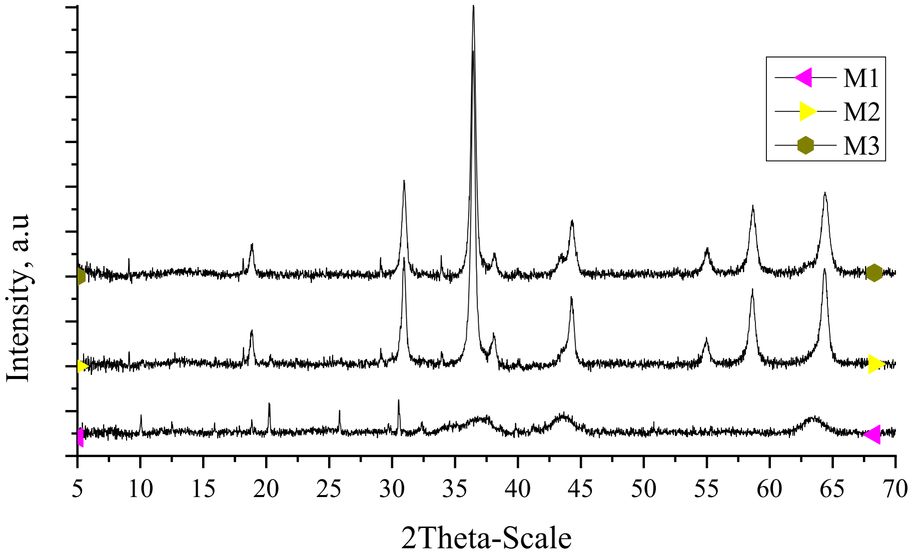

Fig. 4 WAXRD patterns of NiGaCo/MSO catalysts after reduction

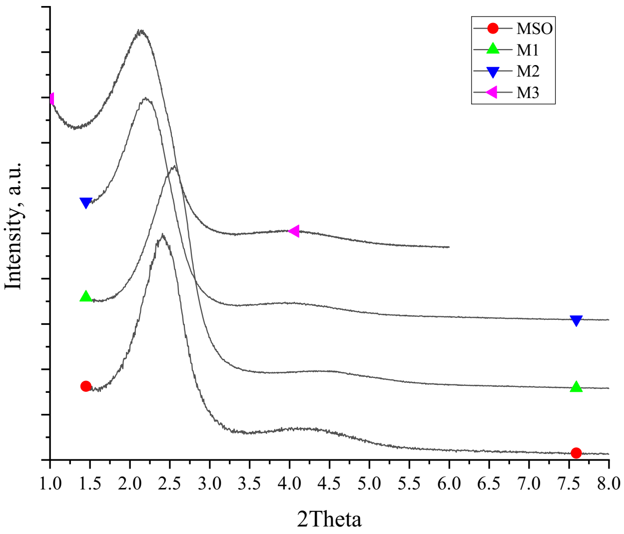

Fig. 5 SAXRD patterns of NiGaCo/MSO catalysts

crystallinity of the M2 sample was the highest, it was chosen for further application in the conversion of CO_2 to methanol.

The FT-IR spectra of the catalysts indicated very similar specialized peaks for meso-SiO_2 support and NiGaCo based alloys at the wavenumbers of ~ 3400 cm^{-1}, ~ 2050 cm^{-1}, ~ 1400 cm^{-1}, ~ 700 cm^{-1} and ~ 500 cm^{-1}, as being noted in the Fig. 6 [17, 21–23]. In which, the –OH, Si–O and Si–H signals characterized the amorphous silica support (MSO), the Ni–Ga and Ga–Co signals indicated the alloy existence in the catalyst, and the Ga–O described either the non-reduced Ga_2O_3 of the Ni–Ga–Co system or the connection between Ga metal and the MSO support. The FT-IR spectra confirmed the appearance of the bonding connection between alloy phases in the metals and the support.

BET surface area measured for the catalyst M2 reached 325.555 m²/g which was high enough for diffusing the active metal alloy sites. Compared to the BET surface area of the MSO support (395.20 m^2/g), there was a small decrease in the BET surface area of the M2 catalyst caused by the cover of the metal sizes onto the support's surface. The adsorption–desorption isotherm also confirmed the mesoporous texture occured in the catalyst (Fig. 7). The isotherm was very specified for a mesoporous material with a hysteresis loop occurred between the adsorption and desorption curves, caused by the gas condensation within the mesoporous channels [17, 21, 23]. Pore distribution of the M2 catalysts was also plotted in Fig. 8, calculated by BJH method.

The BJH results illustrated that the mesoporous channels in the M2 catalyst were ordered, and the porewidth concentrated at around 3.5 nm which very similar to other typical materials [17, 21, 23].

Behaviour of the catalyst during the reduction could be estimated through H_2-TPR technique. In this report, the TPR technique was measured by establishing TG–DSC–MS method under hydrogen flow atmosphere. The results obtained from the TG–DSC were plotted in Fig. 9 where mass and heat flow were plotted against temperature.

The observation in Fig. 9 exhibited three mass loss ranges on TGA diagram, consisting of before 150 °C, from 150 to 625 °C, and from 625 to 800 °C, corresponding to water removal, reduction of different metal alloy sites, and condensation along with reduction, respectively. The reduction

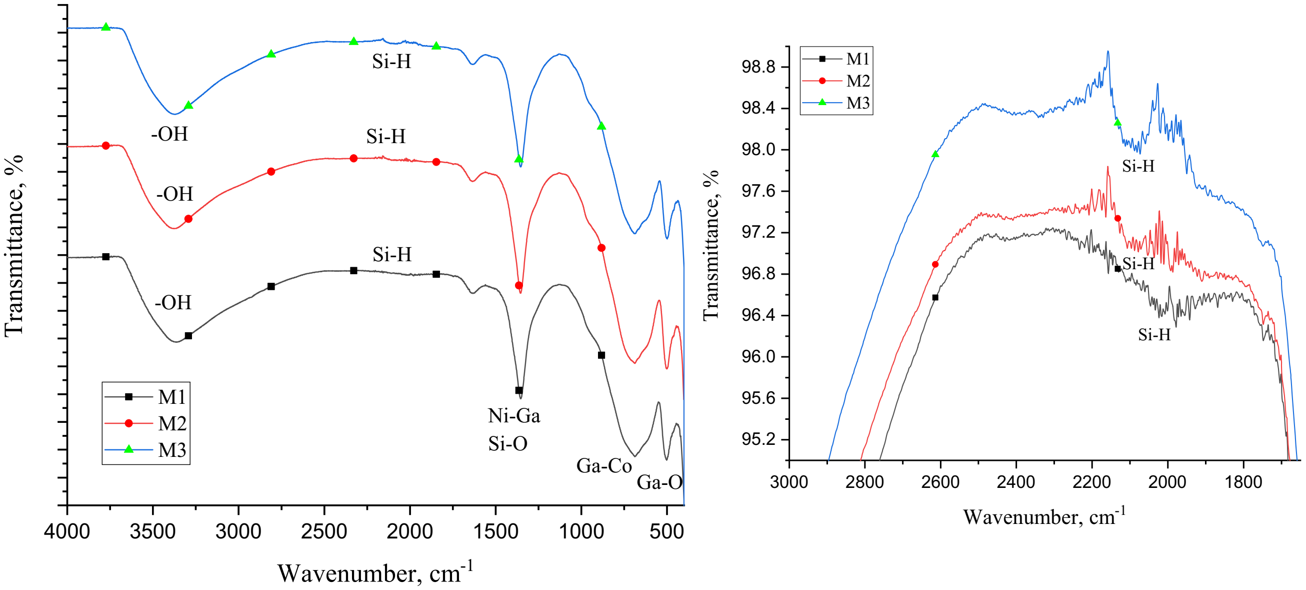

Fig. 6 FT-IR spectra of catalysts and their zoomed spectra on 3000–1650 cm^{-1} wavenumber range

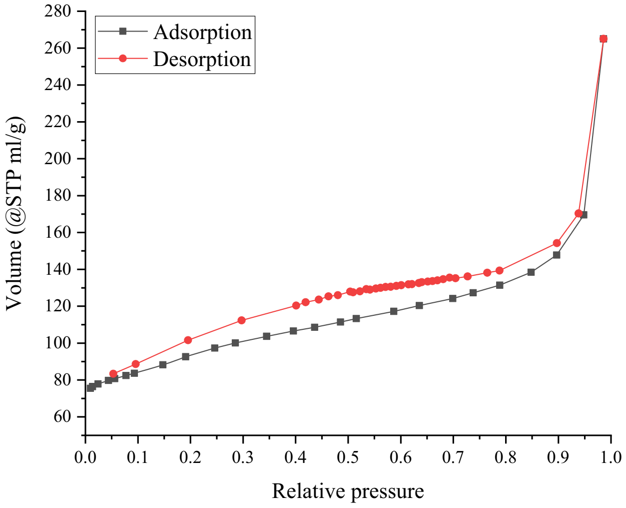

Fig. 7 Adsorption–desorption isotherm of M2 catalyst

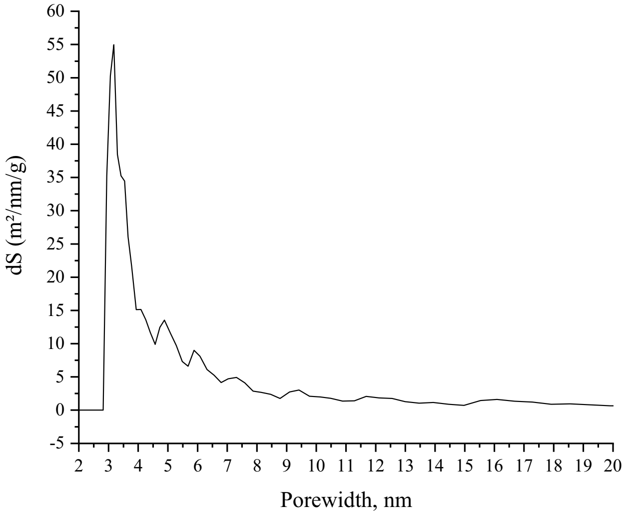

Fig. 8 BJH pore distribution of M2 catalyst due to its specific surface area

reactions were well confirmed through large exothermic effect in the DSC diagram. The exothermic peak appeared at around 550 °C which could be assigned for the strongest reduction occurred at this temperature. However, information obtained from the TG–DSC diagram was not enough to point out which type of sites being reduced at a certain temperature. Therefore, MS was applied to clarify this information by detecting the gas emitted from the TG–DSC method. The MS spectra for the gase were plotted from Fig. 10 because no other gases were detected.

According to the results obtained from the Fig. 10, there were three temperature peaks of water emitted from the TG–DSC, at around 100 °C, 450 °C and 580 °C. These temperatures could be assigned for the water removal and

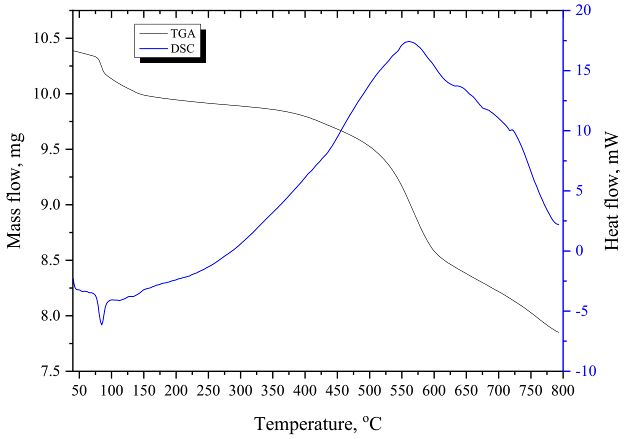

Fig. 9 TG–DSC diagram of M2 catalyst

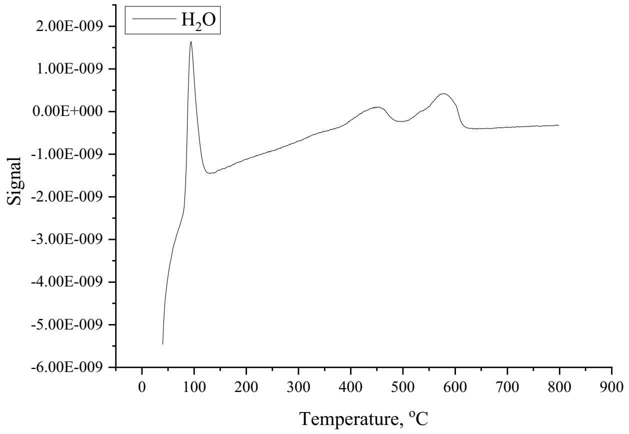

Fig. 10 MS signal of water at different temperature

the reductions of metal alloy at different temperatures. The reduction at 450 °C and 580 °C represented to the alloy sites connected to the MSO support with medium and strong contact [17, 21], and no evidence was observed for the reduction of the alloy sites which had no connection to the support. Along with this connection, the high reduction temperatures also supported the positive role of Co as a promoter. All these reasons considerably strengthened the diffusion of the Ni_5Ga_3 active site and avoided them to be coaggulated at high temperature.

XPS spectra in total and partial ranges were plotted in Figs. 11, 12, 13, 14 and 15. Results demonstrated that the Ga signals in the M2 catalyst were metal and alloy state at bond energies of 1116.5 eV and 1140.5 eV, respectively. There was no signal of the Ga_2O_3 illustrating that the reduction of the catalyst in the $NaBH_4$/ethanol solution was highly effective in transforming Ga^{3+} to Ga° [12].

XPS spectra for Ni sites showed that Ni metal existed at bond energies of 875.5 eV, 869.3 eV, 857.8 eV and

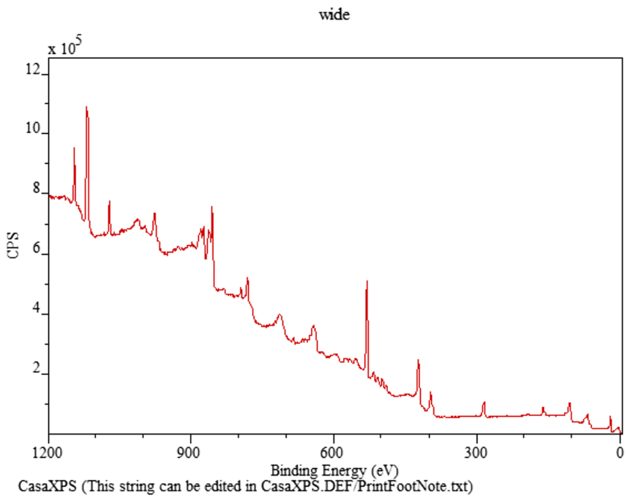

Fig. 11 XPS spectra of M2 catalyst

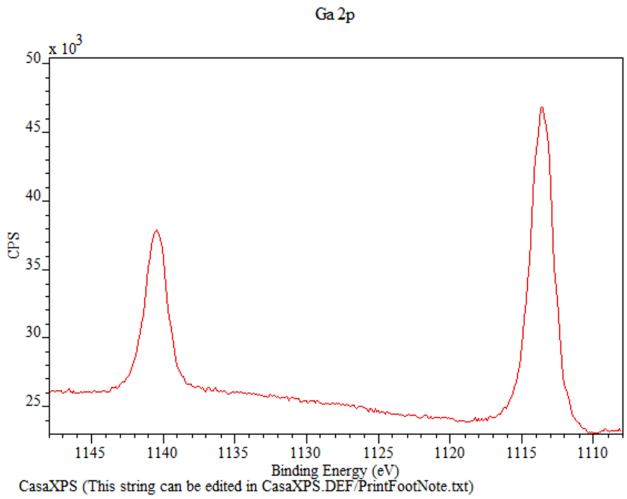

Fig. 12 XPS spectra of Ga_{2p} site in M2 catalyst

851.7 eV corresponding to Ni metal connected with support through oxygen bridges, Ni in alloy state with Co, Ni metal and Ni in alloy state with Ga, respectively. There was no trace for Ni in oxide state, so the whole Ni^{2+} was reduced to Ni^{o} after treatment with $NaBH_4$ 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 characterized for the Ni connected with the MSO support [12].

XPS spectra of Co site showed peaks in 792.1 eV and 777.0 eV assigned for Co in alloy state with Ni and Co metal, respectively. There was also no existence of the CoO peaks demonstrating that the Co^{2+} was totally reduced to Co metal.

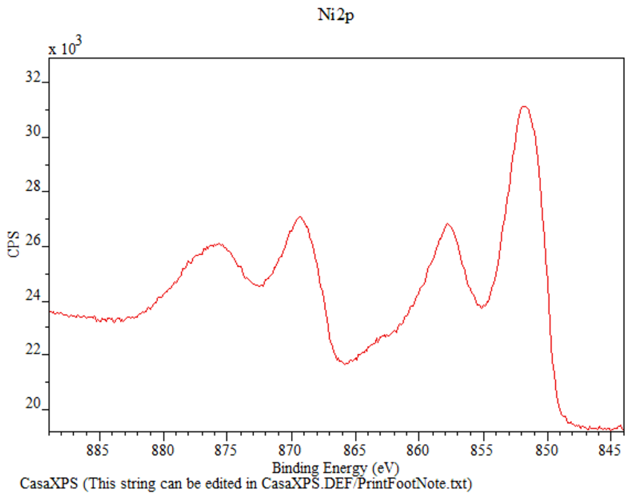

Fig. 13 XPS spectra of Ni_{2p} site in M2 catalyst

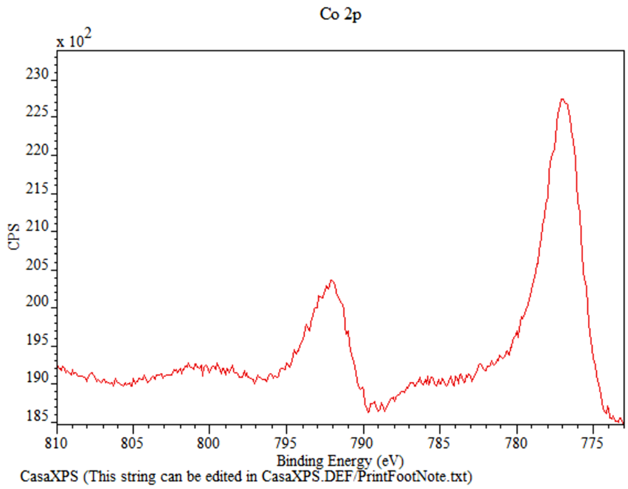

Fig. 14 XPS spectra of Co_{2p} site in M2 catalyst

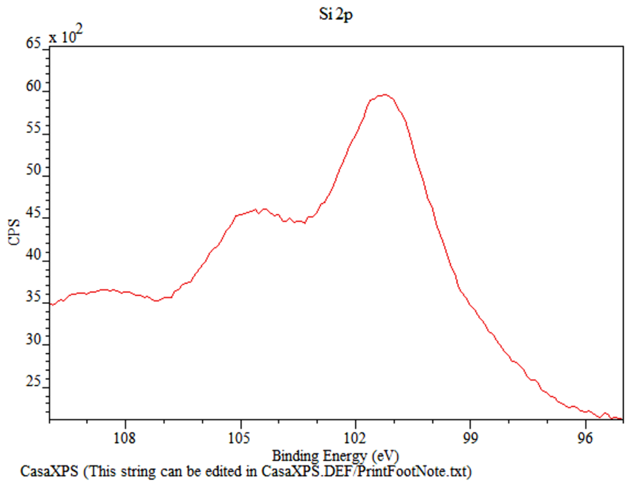

Fig. 15 XPS spectra of Si site in M2 catalyst

XPS spectra of Si site sharply indicated signal of silica SiO_x at bond energies of 104.6 eV and 101.2 eV. There was an energy shift to the higher value compared to normal silica [12, 17] 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.

3.3 Activity of Ni–Ga–Co/MSO catalyst in conversion of CO_2 to methanol

For the activity comparison, the conversion of CO_2 to methanol process was established in both low and high pressure conditions. As mentioned previously in another report [17, 23], using NiGa/MSO catalyst, 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 H_2/CO_2 volume ratio of 3/1. In such conditions, the conversion of CO_2 and the selectivity of CH_3OH were 46.9% and 62.7%, respectively. The yield of the whole process was 29.4%.

Investigations of the CO_2 conversion process over NiGaCo/MSO catalyst were conducted by the same steps as being conducted over the NiGa/MSO catalyst [17, 23]. Results obtained from the process established at 35 bars and 5 bars were plotted in Figs. 16 and 17, respectively.

Results exhibited that the CO_2 conversions for the processes over the Ni–Ga–Co/MSO and Ni–Ga/mesosilica were 52.0% and 46.9% respectively, which pointed out that there was an increase in the CO_2 conversion after modifying the catalyst. Results exhibited that the methanol selections for the processes over the Ni–Ga–Co/MSO 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/MSO was higher than that of the Ni–Ga/mesosilica catalyst.

In low pressure of 5 bars, although the conversion of CO_2 sharply decreased compared to the case of 35 bars, the

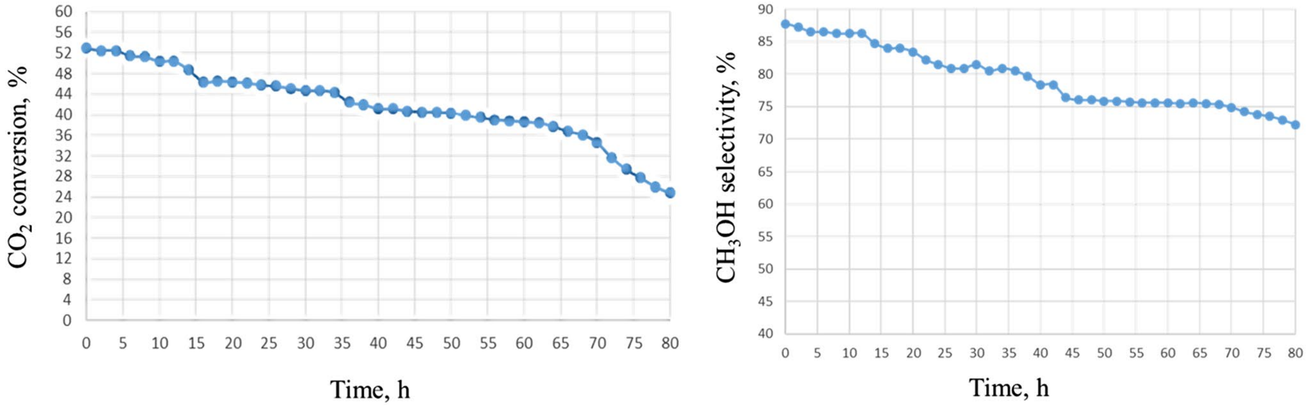

Fig. 16 CO_2 conversion and methanol selection at pressure of 35 bars

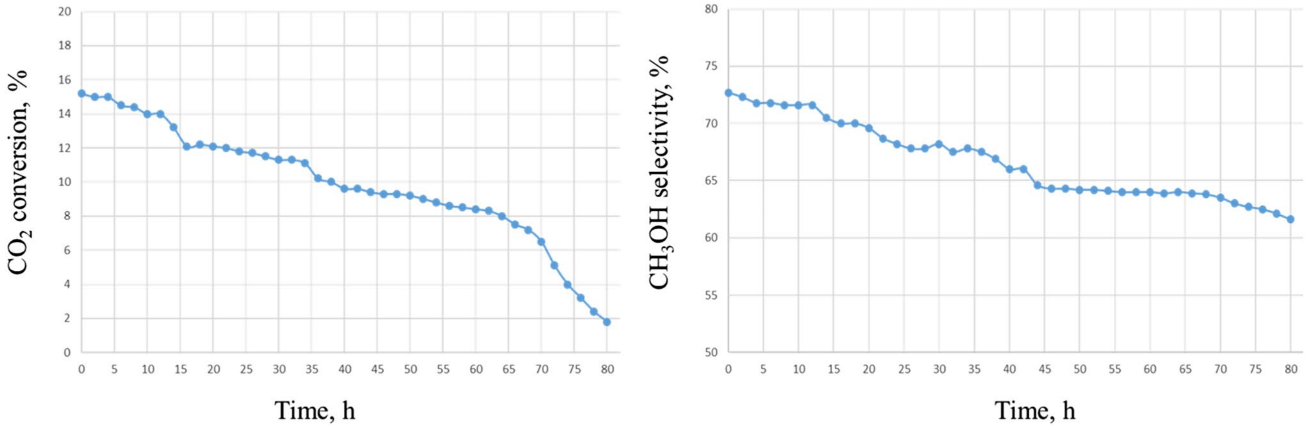

Fig. 17 CO_2 conversion and methanol selection at pressure of 5 bars

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 sharply enhanced the catalytic performance in the conversion of CO_2 to methanol process. On the whole, the process conducted over the Ni–Ga–Co/MSO catalyst achieved some major results: pressure of 35 bars, temperature of 270 °C, CO_2 conversion of 52%, methanol selection of 85%, catalysis life-span of 70 h.

4 Conclusion

Ni–Ga–Co/MSO catalyst possessed ordered mesoporous structure with high thermal and hydrothermal stability, good surface area with focused pore width and homogeneous metal distribution derived from a layered structure like matrix. Especially, the Ni_5Ga_3 active site for the CO_2 conversion to methanol was stabilized by connections with Co and the MSO support enhancing its activity and stability in the synthesis of methanol.

The investigations of the methanol synthesis process clearly illustrated the high activity and selectivity of the catalyst. The life spans of the catalyst at 35 bar and 5 bar were also estimated by the time that the catalyst was exposed in the reaction flow. The results showed that the catalyst activity could be stable after 70 h of reaction.

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