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ISSN: 2278-1862

Journal of Applicable Chemistry

2019, 8 (4): 1825-1837

(International Peer Reviewed Journal)

Investigation of CO_2 to CH_3OH Conversion Process over NiGa/mesosilica Catalyst

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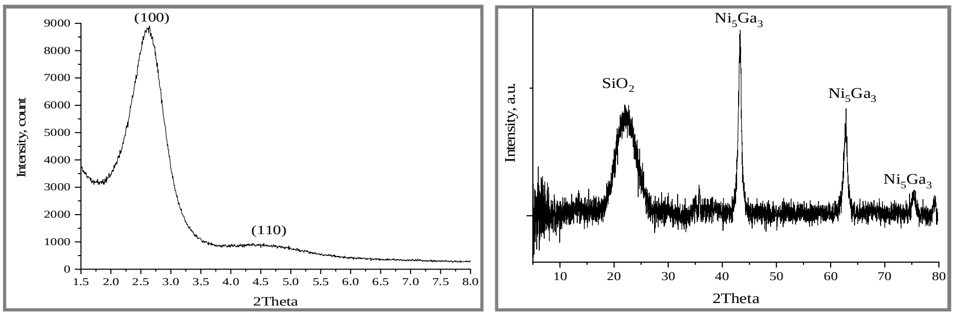
Accepted on 30th May, 2019

ABSTRACT

In this study, investigations of CO_2 to CH_3OH conversion over NiGa/mesosilica catalyst were established for determining a set of suitable parameters applied in the process. There were four parameters which were considered including effects of temperature, time, pressure and H_2/CO_2 volume ratio. The novel NiGa/mesosilica catalyst prepared and characterized in elsewhere study possessed high surface area, ordered mesoporous structure and high active sites of Ni_5Ga_3 which considerably improved the performance of this reaction. The results exhibited an excellent activity and stability of the NiGa/mesosilica catalyst compared to many other studied catalysts, and the high yield of CH_3OH opened a novel and effective way of direct conversion of CO_2 to utilizable products. The Gas Chromatography coupled with Thermal Conductivity Detector (TCD) and Flame Ionization Detector (FID) was applied for analyzing the gas products composition.

Graphical Abstract



XRD patterns of NiGa/mesosilica catalyst

Highlights

- Preparing and characterizing NiGa/mesosilica catalyst: the catalyst possessed high surface area, ordered mesoporous structure and high active sites of Ni_5Ga_3 which considerably improved the performance of this reaction;
- Investigating conversion of CO_2 to CH_3OH in continuous flow system: the results exhibited an excellent activity and stability of the catalyst through the high yield of CH_3OH.

Keywords: Methanol economy, Carbon dioxide reduction, NiGa based catalyst, Mesoporous materials.

INTRODUCTION

Methanol played a crucial role in modern industrial economy for its advanced characteristics and potential of applications such as: blending with gasoline because of its high octane number, producing fuel cell; synthesizing dimethyl ether (DME) as a diesel additive; converting to many important chemicals, especially olefins for chemical synthesis industry; etc. In fact, some researchers pointed out that methanol would be considered as the most important chemical for the future chemistry production-the Methanol Economy [1-4]. However, producing methanol from syngas, the most popular process today, expensed a large amount of energy and fossil sources, especially coal [1, 5-8]. Therefore, reducing the cost of the methanol production by direct conversion in one-step processes could be considered as the most effective way to enlarge the scale of methanol production [1, 2, 8, 9]. Carbon dioxide was indicated as the most suitable candidate for such processes, and the direct conversion of carbon dioxide to methanol would be the hottest trend in methanol synthesis and production in the future [10-12].

NiGa alloy based catalyst was introduced recently for its good activity and selectivity in the conversion of CO_2 to methanol [8]. The study reported that the methanol synthesis could be effectively established at mild conditions over the NiGa alloy because of its existence of Ni_5Ga_3 active sites which possessed excellent activity with the process. However, the stability of the NiGa alloy was an open question because the active site Ni_5Ga_3 could be easily agglomerated at the conditions of the conversion, and it was demonstrated and confirmed by our studies in recently published report [18, 19]–the life span and even the activity of the NiGa alloy were low because of low distribution of the Ni_5Ga_3 sites. Many efforts of us were spent for enhancing the activity and stability of the NiGa based catalyst including the introductions of NiGa/mixed oxide and NiGa/mesoporous silica (NiGa/mesosilica) catalysts, and the results showed that the NiGa/mesosilica catalyst showed the highest performance in the process [18]. This was caused by its high surface area, concentrated ordered mesoporous channels and good distribution of Ni_5Ga_3 active sites on mesosilica support. The demonstrations for its catalytic structure were completed, but the whole investigations of the methanol synthesis were still under research.

In this report, we completed these investigations by applying the NiGa/mesosilica catalyst in the direct conversion of CO_2 to methanol with varying the most important parameters of this process such temperature, time, feedstock composition and pressure. The results obtained from this study could contribute a good base for the applications of the catalyst in the future.

MATERIALS AND METHODS

Chemicals: Chemicals used in the study such as $Ni(NO_3)_2.6H_2O$, $Ga(NO_3)_3.9H_2O$, concentrated HNO_3 63%,NaOH, $NaBH_4$, TEOS and CTAB were purchased from Merck, Germany and were used with no further purification. Deionized water was prepared at local lab. Hydrogen and CO_2 were ordered domestically and met technical characteristics for the reactions.

Preparation of NiGa/mesosilica catalyst: The preparation of the NiGa/mesosilica catalyst was published in another report [18] including two main steps: synthesis of the mesoporous amorphous silica support (mesosilica) through self-assembly condensation method, and formation of the NiGa/mesosilica catalyst through impregnation method. The NiGa/mesosilica catalyst possessed ordered mesoporous channels, high surface area of 437.3 m^2/g, high thermal stability and active sites of Ni_5Ga_3. The catalyst was applied in the conversion of CO_2 to methanol in both circumstances: mild and high pressure. Some characterization such as SAXRD, WAXRD and XPS were applied for confirming the catalysts porous structure.

Investigations of CO_2 to methanol conversion process: The process was established using Altamira AMI-902 catalyst activity test system in Petrovietnam Research and Development Center for Petroleum Processing (PVPro), Ho Chi Minh city, Viet Nam. The reactions were considered in the process including conversion of CO_2 to methanol, conversion of CO_2 to CO and conversion of $CO_2$to methane.

Conversion under mild pressure: The reactor in the investigations was fix-bed catalyst type made of high quality quartz tube with inner diameter of 6 mm. The tube was connected to gas tubing, electric heating chamber for providing the system with exact gases and temperatures. The outlet of the quartz tube was connected directly with Agilent 7890A gas chromatography machine coupled with Thermal Conductivity Detector (TCD) and Flame Ionization Detector (FID) for analyzing inorganic and organic compounds, respectively. The gas samples were periodically withdrawn for the analysis, and the results (gas composition) were collected after five times of measurement. Yield of the process could be calculated from the conversion of CO_2 and selectivity of the produced methanol.

The investigations were based on these parameters: catalyst volume of 1 mL, firstly was reactivated at 350°C for 3 h under H_2 flow of 30 mL min^{-1}, the reactions were established under a gas mixture of 25% CO_2 + 75% H_2 by volume; the total gas flow was 100 mL min^{-1} corresponding to the volume space velocity of 6000 h^{-1}, the temperature was changed from 100°C to 510°C.

Conversion under high pressure: Conversions of CO_2 to CH_3OH at higher pressures were conducted. Procedures for the high pressure process were the same as for the low pressure one except raising the pressure of the system from 10 bars to 50 bars, the temperature from 100°C to 510°C and H_2/CO_2 volume ratios from 1/1 to 5/1. The time for the process was investigated continuously in 60 h. By this way, the catalyst's activity and stability were both indicated. Gas samples were withdrawn after each 1 h of the reaction for analysis by GC-TCD-FID method.

RESULTS AND DISCUSSION

Structure of NiGa/mesosilica catalyst: Ordered mesoporous structure of the NiGa/mesosilica catalyst was characterized by SAXRD pattern plotted in figure 1, and WAXRD pattern of the catalyst in figure 2 could demonstrate the occurrence of the Ni_5Ga_3 active sites (crystalline) over the amorphous silica. Element composition and chemical states of Ni and Ga in the catalyst were demonstrated by XPS analyzed in figure 3 and figure 4.

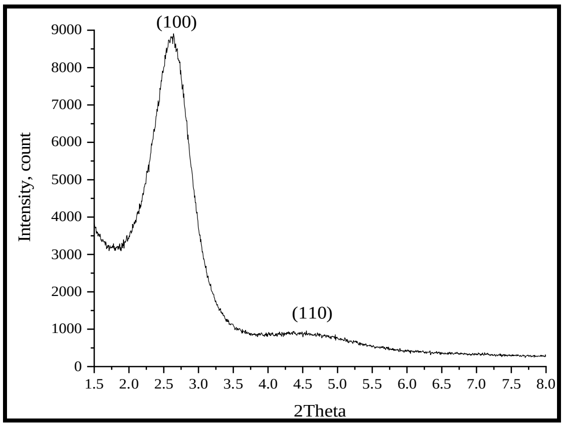


Figure 1. SAXRD pattern of NiGa/mesosilica catalyst.

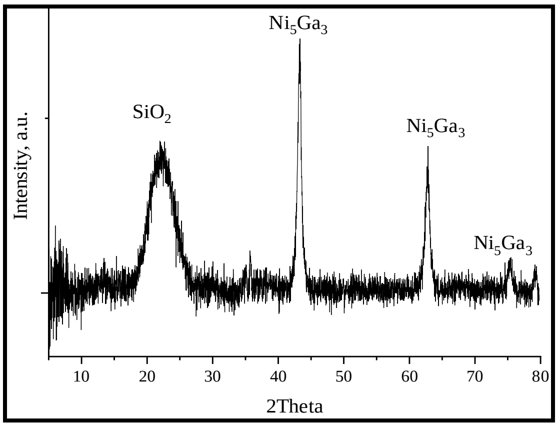


Figure 2. WAXRD pattern of NiGa/mesosilica catalyst.

The SAXRD pattern of the NiGa/mesosilica catalyst clearly confirmed its ordered mesoporous structure through existence of the fingerprint peak at 2 theta ~ 2° corresponding to the diffraction signal of the (100) planes. The peaks distinguish and intensity was high proving that the impregnation of Ni and Ga on the mesosilica support did not destroy or dramatically change the mesoporous structure. This brought a high specific surface area and uniform mesoporous channels for enhancing the distribution of the active sites [20, 21]. The WAXRD pattern of the NiGa/mesosilica catalyst undoubtedly indicated the existence of the crystalline Ni_5Ga_3 active phase besides the amorphous silica background. There was no trace of any other crystalline phase illustrating the success of introducing the active sites into the mesosilica support. This structure could contribute to the stability of the Ni_5Ga_3 active sites because of the porous structure of the mesosilica [8].

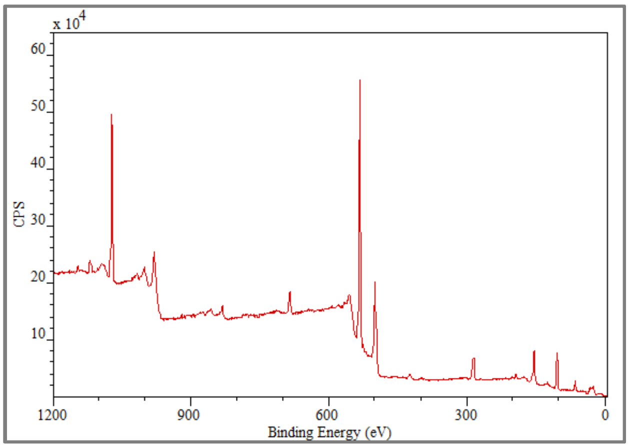


Figure 3. XPS wide diagram of NiGa/mesosilica catalyst.

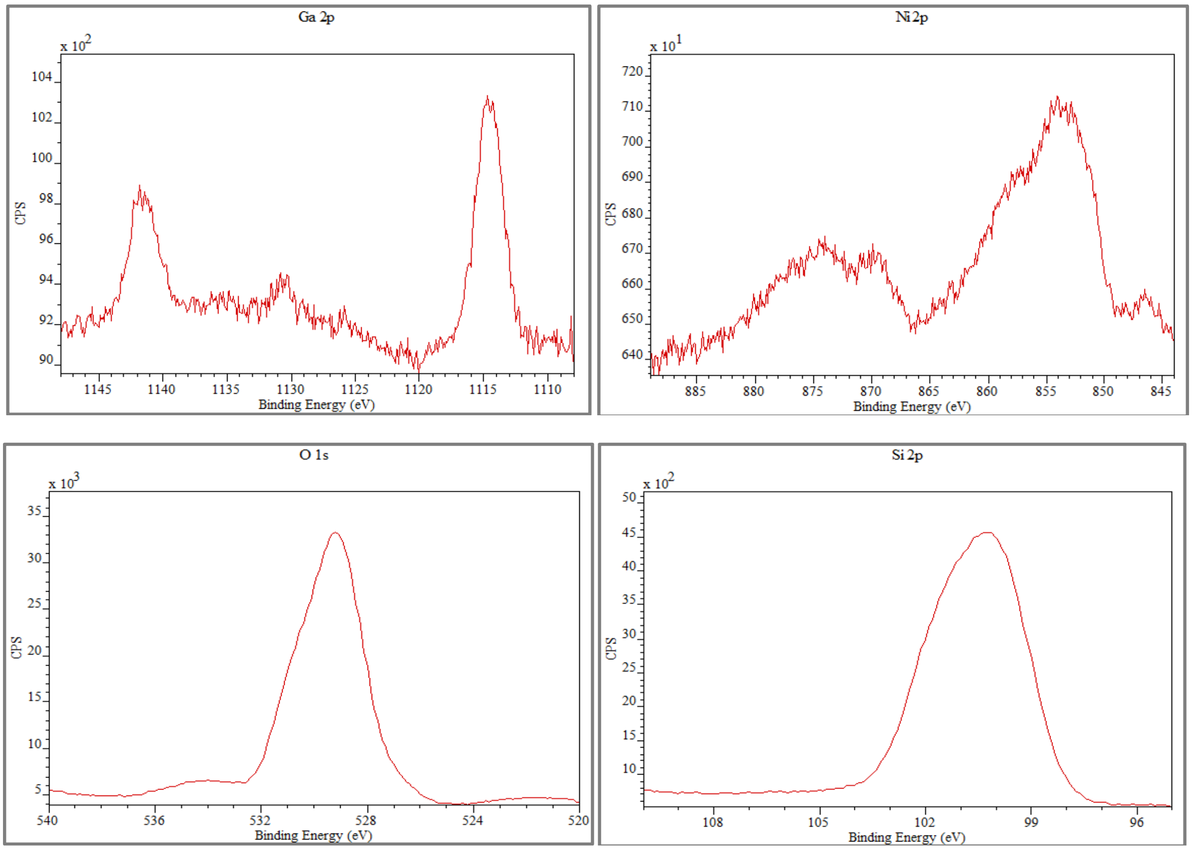


Figure 4. XPS element diagrams of NiGa/mesosilica catalyst.

According to many studies [8, 13-16], the signals for Ga_{2p} and Ni_{2p} clearly proved that they were all in metal states. Because of the existence of the only Ni_5Ga_3 crystalline phase in WAXRD pattern, that was reasonable to conclude that all metal states in the catalyst belonged to the Ni_5Ga_3 alloy. The binding energies for each element were also easily observed. On the other hand, there were surely an appearance of O and Si peaks because the mesosilica took a large amount in the catalysts composition. The Ni_5Ga_3 was also the favorable active sites required for the conversion of CO_2 to methanol.

Investigation of CO_2 to CH_3OH conversion process at mild pressure: Because the process was established at atmospheric pressure (1 bar), temperature played a very important role to its performance. Table 1 showed results obtained from the analysis of the gas product composition at different process's temperatures. By these values in the table 1, a series of diagram could be extracted from, and they were all showed in figure 5 and figure 6.

Table1. Gas composition of product obtained from CO_2 conversion at mild pressure

T °C	H_2	CO_2	CO	CH_4	C	CH_3OH
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

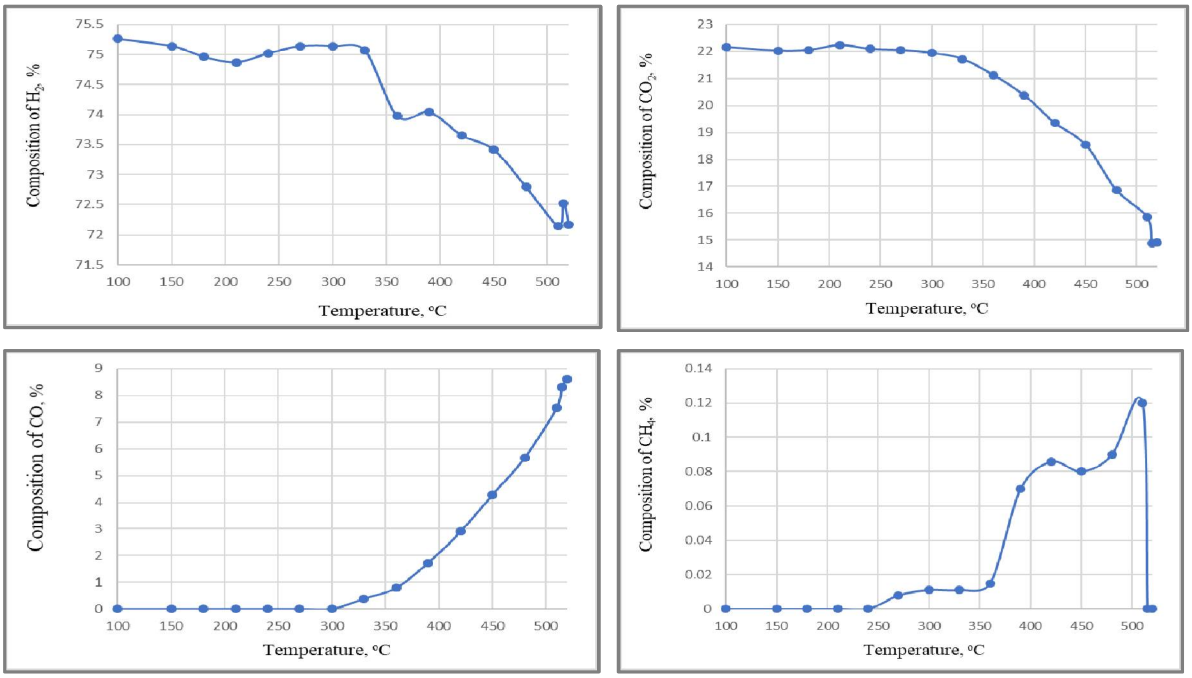


Figure 5. Gas composition in product of CO_2 conversion process over NiGa/mesosilica catalyst at mild pressure.

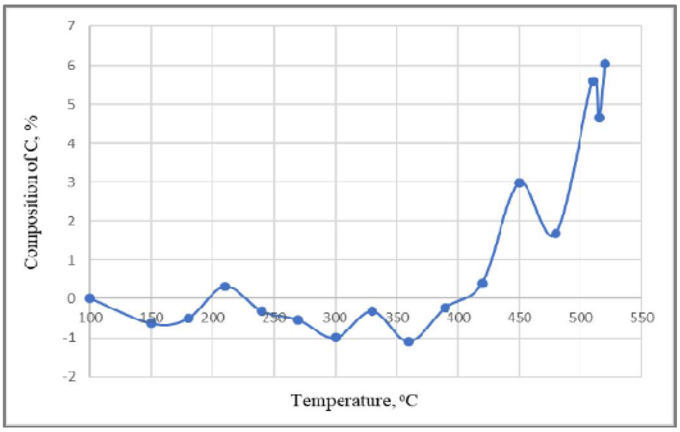


Figure 6. Carbon composition in product of CO_2 conversion process over NiGa/mesosilica catalyst at mild pressure

The plotted and calculated results clearly showed that, at low pressure, CO_2 could be converted to many products such as CO, CH_4 and C except CH_3OH – the desired product. On the other hand, content of the by-products such as CO, CH_4 and C was sharply increased at high temperature over 400°C. Especially the C content rose dramatically at the temperature higher than 420°C, and it should be avoided because the catalyst could be poisoned when being exposed to such high content of condensed carbon. Because the results showed a very poor performance in the production of methanol, the low pressure was not appropriate for the whole process. The process was therefore introduced to other procedures carried out at higher values of pressure.

The reason for the low performance of the catalyst at low pressure could be explained by the thermodynamic characteristics of the main reaction. The conversion of CO_2 to CH_3OH belonged to volume-decrease reaction which should be accelerated at high pressure for shifting the direction to the methanol generation side.

Investigation of CO_2 to CH_3OH conversion process at higher pressures: The investigations of the process could be considered on two main targets: conversion of CO_2 and selectivity of CH_3OH. Both of them could be easily calculated from the gas's composition of the outlet streaming. There were four important parameters which were investigated in the study including temperature, pressure, time and H_2/CO_2 volume ratios. In the former three parameters, because the gas composition would covariate with the conversion of CO_2 and the selectivity of CH_3OH because they were all based on the same feedstock composition. The consequence was that the investigations of these parameters could base on either gas composition or conversion of CO_2 and selectivity of CH_3OH. It could be more convenient for the investigations based on the gas composition. The H_2/CO_2 volume ratio investigations had to be based on the conversion of CO_2 and the selectivity of CH_3OH because of the different volume composition of feedstock.

Effect of temperature: The investigations were established from 100°C to 510°C while fixing other parameters such as pressure of 25 bars, H_2/CO_2 volume ratio of 3/1. Results of the process were collected and plotted in table 2 and figure 7 and figure 8, respectively.

Results obtained from table 2, figure 7 and figure 8 clearly indicated common trends in the gas composition due to the reaction's temperature: increasing the temperature led to decreasing the compositions of H_2 and CO_2 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 CH_4 was still very restricted; the composition of methanol varied at different temperature and reached peak at 270°C; at higher temperature, the selectivity for methanol decreased.

At the first sight, it could be said that the process established at 25 bars became much more effective than being established at atmospheric pressure. It could be also based on the thermodynamic of such reactions for a reasonable explanation: because the reaction (1) was volume-decreased and exothermic, it could be favorable for implementing the process at high pressure and high enough temperature; the investigation showed that the best temperature for this process was of 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 [13-15]. On the whole, the temperature of 270°C was favorable for the investigation, in which the methanol content reached 8.59% by volume, and the CO,

Table 2. Effect of temperature on gas composition in conversion of CO_2 to CH_3OH

T, °C	H_2, %	CO_2, %	CO, %	CH_4, %	CH_3OH, %
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

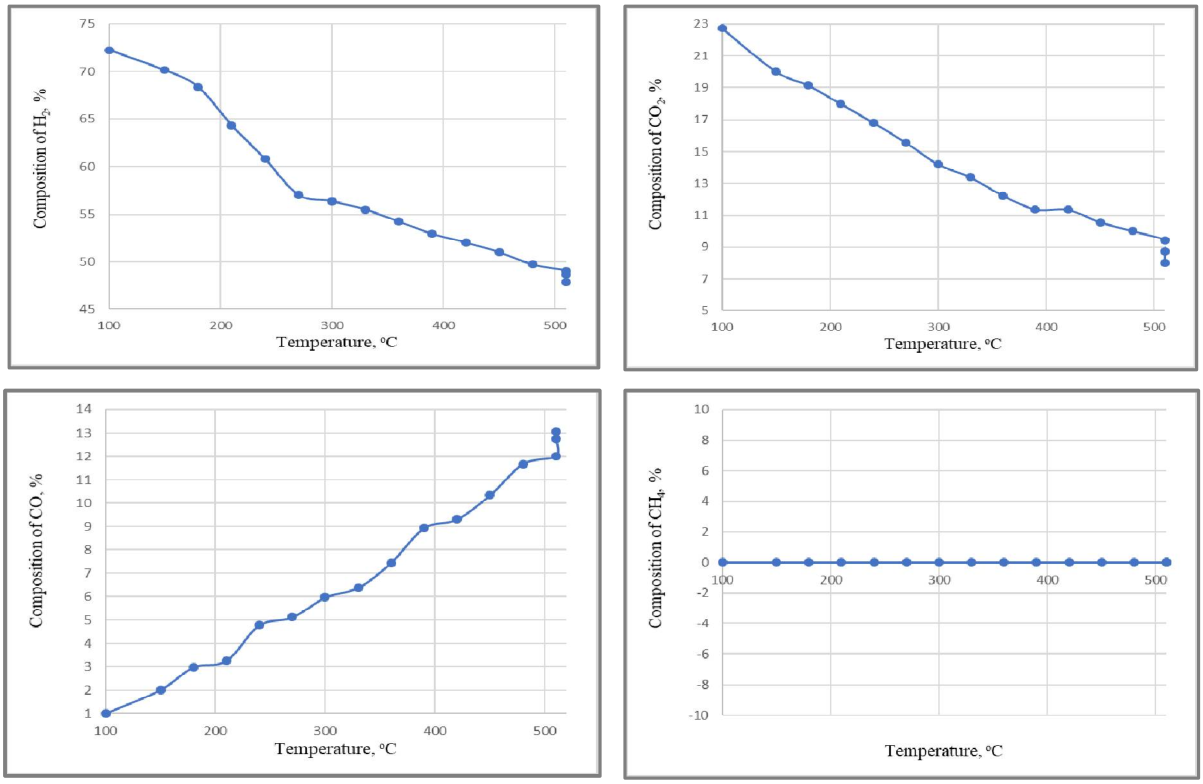


Figure 7. Effect of temperature on gas composition in conversion of CO_2 to CH_3OH.

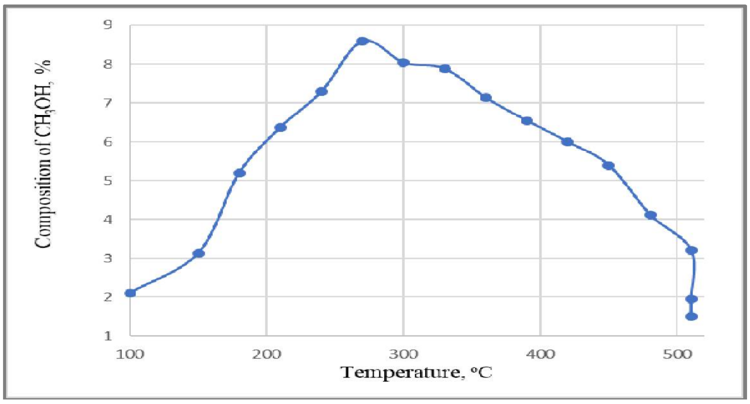


Figure 8. Effect of temperature on methanol composition in conversion of CO_2 to CH_3OH.

CH_4 generations were limited well; especially, there was no carbon formation was a good behavior because it could well improve the catalyst's stability.

Effect of pressure: The pressure of the process changed from 10 bars to 50 bars while other parameters were kept such as temperature of 270°C, H_2/CO_2 volume ratio of 3/1. Results of the process were collected and plotted in table 3 and figure 9 and figure 10, respectively.

Table 3. Effect of pressure on gas composition in conversion of CO_2 to CH_3OH

P, bar	H_2, %	CO_2, %	CO, %	CH_4, %	CH_3OH, %
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

The profile relating to the effect of pressure on such process was different from the effect of temperature: the composition of CO_2 and H_2 decreased from 10 bars to 35 bars and became stably after that; the CO composition slowly increased and also became constantly after reaching 35 bars, and there was still no trace of CH_4 in the outlet gas components; the methanol composition gradually increased from 10 bars to 35 bars and also was constant at higher pressure.

Explanations for these results were also rooted from the thermodynamic properties of the reaction (1) and (2) which were volume-decreased and constant volume, respectively. The equation (1) would shift in 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^{o}C. The 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 because the decrease of the volume of the feedstock and the whole process. The pressure of 35 bars was suitable for the process.

Effect of H_2/CO_2 volume ratio: The stoichiometry of the equation (1) was $H_2:CO_2$ = 3:1, so the investigations of the H_2/CO_2volume 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 fixing other parameters such as temperature and pressure at 270^{o}C and 35 bars, respectively.

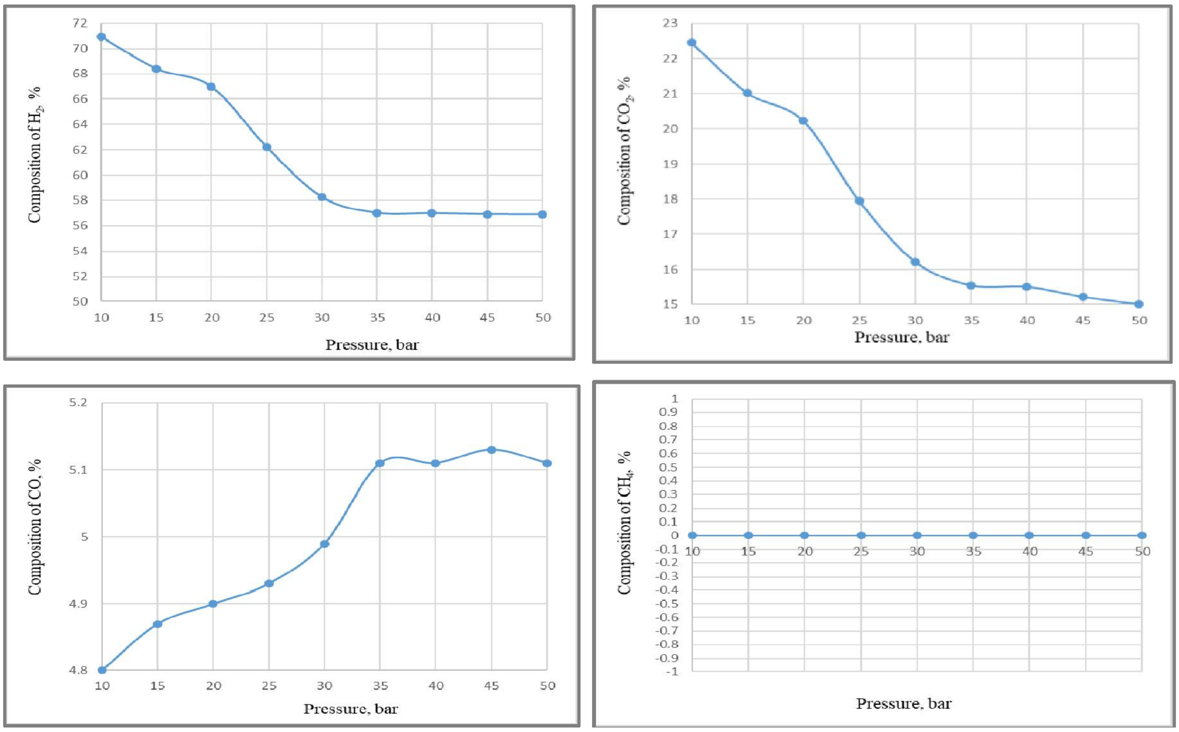


Figure 9. Effect of pressure on gas composition in conversion of CO_2 to CH_3OH.

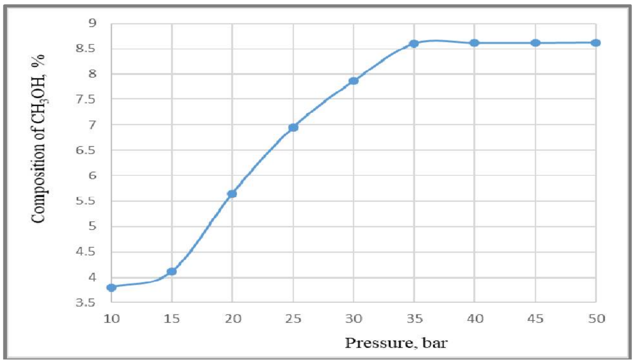


Figure 10. Effect of pressure on m composition in conversion of CO_2 to CH_3OH.

Because of the changes in feedstock composition, the outlet gas composition would not precisely reflect the variations of CO_2 conversion as well as CH_3OH selectivity. In this case, the CO_2 conversion and CH_3OH selectivity could be considered as the main factors for the investigation. The results of the investigation were collected in table 4 and plotted in figure 11.

Table 4. Effect of H_2/CO_2 volume ratio on gas composition in conversion of CO_2 to CH_3OH

H_2/CO_2	CO_2 conversion, %	CH_3OH selectivity, %
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

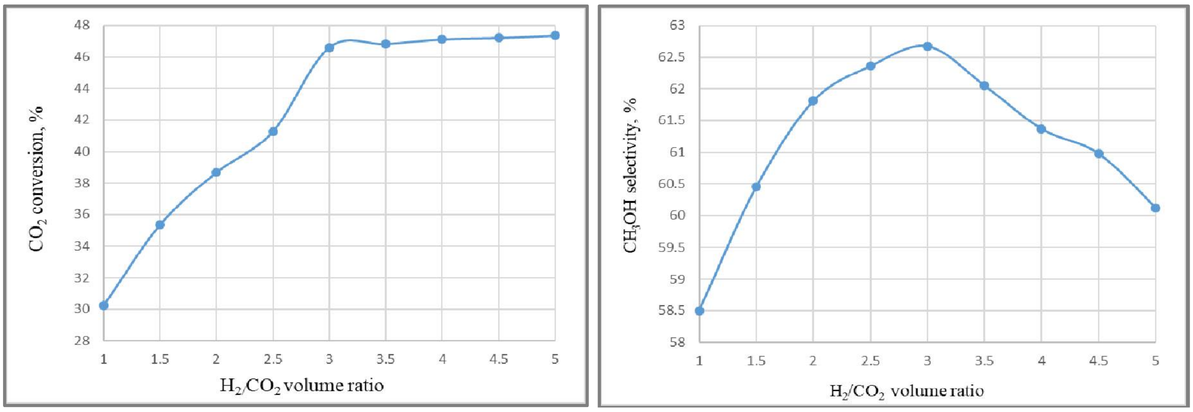


Figure 11. Effect of H_2/CO_2 volume ratio on gas composition in conversion of CO_2 to CH_3OH.

The investigations showed that increasing the H_2/CO_2volume ratio could raise the CO_2 conversion to a high and stable value. In contrast, the profile of the CH_3OH selectivity could reach a peak at the ratio of 3/1. These were also caused by the thermodynamic characteristic of the equation (1) and (2). When the volume ratio was high, there was an excess of H_2 in the process yielding the shift of equation (1) and (2) into the direction of increasing the CO_2 conversion. However, the conversion could only reach the highest value of ~ 47%. The selectivity of CH_3OH also accelerated when the volume ratio of H_2/CO_2 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 H_2/CO_2.

Hence, the H_2/CO_2 volume ratio applied for the process should be 3/1 for enhancing both of the CO_2 conversion and CH_3OH selectivity. These values achieved 62.68% for the former and 46.62% for the later parameters meaning the CH_3OH yield of the whole process of 29.22%. Compared to many other studies [**8, 13, 17**], the CH_3OH yield was much higher demonstrating the good activity of the NiGa/mesosilica catalyst.

Effect of time: There was a big difference between the process established by the batch reactor and the process carried out by the continuous reactor [**13, 16**]. In the batch reactor, the process was completed after an exact period of time before the whole products were analyzed for their chemical compositions. In contrast, the continuous process included the reaction and analysis at the same time. Therefore, the investigation of time for the continuous process played in both roles: estimation of the reaction performance, and consideration of the catalyst stability (or the catalyst life span). In this investigation, the results collected and analyzed in table 5 and figure 12 could be applied for the both purposes.

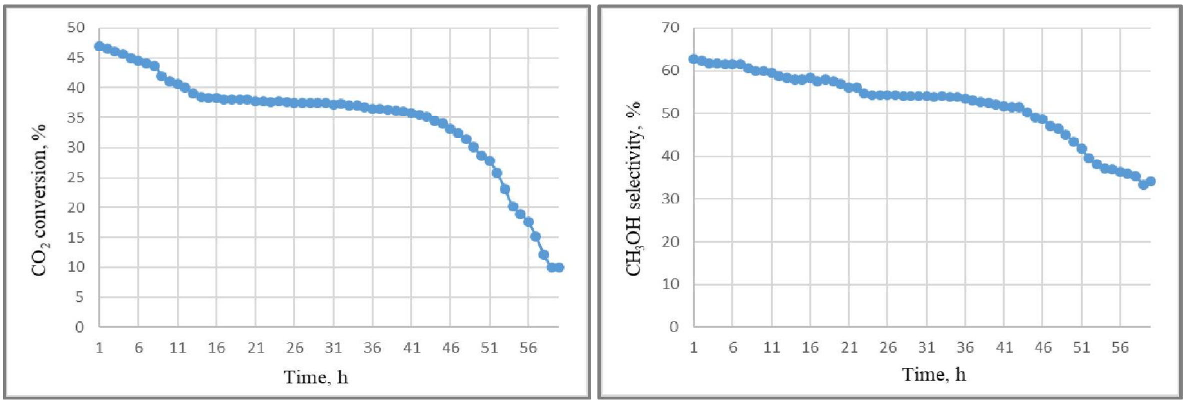


Figure 12. Effect of time on gas composition in conversion of CO_2 to CH_3OH.

Table 5. Effect of time on gas composition in conversion of CO_2 to CH_3OH

Time, h	CO_2 conversion, %	CH_3OH selectivity, %	Time, h	CO_2 conversion, %	CH_3OH selectivity, %
1	46.9	62.7	31	37.2	54
2	46.5	62.3	32	37.3	53.9
3	46.1	61.8	33	37	54
4	45.6	61.8	34	37	53.9
5	44.9	61.6	35	36.7	53.8
6	44.5	61.6	36	36.5	53.5
7	44.1	61.6	37	36.4	53
8	43.7	60.5	38	36.3	52.7
9	42	60	39	36.2	52.5
10	41	60	40	36	52.1
11	40.6	59.6	41	35.7	51.6
12	40.1	58.7	42	35.5	51.4
13	39	58.2	43	35.2	51.4
14	38.5	57.8	44	34.4	50.2
15	38.4	57.8	45	34	49.1
16	38.3	58.2	46	33.2	48.7
17	38.1	57.5	47	32.5	47
18	38	57.8	48	31.4	46.5
19	38	57.5	49	30.1	45
20	38	56.9	50	28.7	43.4
21	37.7	56	51	27.8	41.8
22	37.8	56	52	25.8	39.5
23	37.6	54.6	53	23.1	38.2
24	37.7	54.3	54	20.2	37.1
25	37.6	54.3	55	18.9	36.9
26	37.5	54.2	56	17.6	36.3
27	37.5	54.2	57	15.1	36
28	37.4	54.1	58	12.2	35.4
29	37.4	54	59	10	33.4
30	37.4	54	60	10	34.2

The results obtained from the investigations indicated that the conversion of CO_2 and the selectivity of CH_3OH could both remain their stability until 45 hours of the process reflected by the slight decreases in such values. After 45 hours, the catalyst became less activity corresponding 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^{o}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 selectivity of CH_3OH were of 46.9% and 62.7%, respectively. The yield of the whole process was of 29.4%.**

APPLICATION

Methanol could be a major chemical in chemistry industry for producing other chemicals, products, fuels and various other applications.

CONCLUSION

Investigations of the methanol synthesis from CO_2 at atmospheric and high pressures were established. The results of the synthesis at atmospheric pressure showed poor conversion of the feedstock and selectivity of the main product. This was caused by the restriction in the thermodynamic properties of the synthesis reaction. Therefore, the establishment of the methanol synthesis from CO_2 should be carried out at high enough pressures.

The investigations of the synthesis at higher pressures impressively showed very high activity of the NiGa/mesosilica catalyst. The results showed that the process should be established at temperature of 270^{o}C, pressure of 35 bars, H_2/CO_2 volume ratio of 3/1 and time of 45 hours. The conversion of CO_2 and selectivity of CH_3OH were of 46.9% and 62.7%, respectively, at these conditions, and the yield of whole process was of 29.4%.

ACKNOWLEDGEMENTS

This work was financially supported by the National Foundation for Science and Technology Development, Vietnam (NAFOSTED) under grant number 104.05-2017.21.

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