



## Investigation on Conversion of Carbon Dioxide to Methanol over NiGaCu/MSO Catalyst

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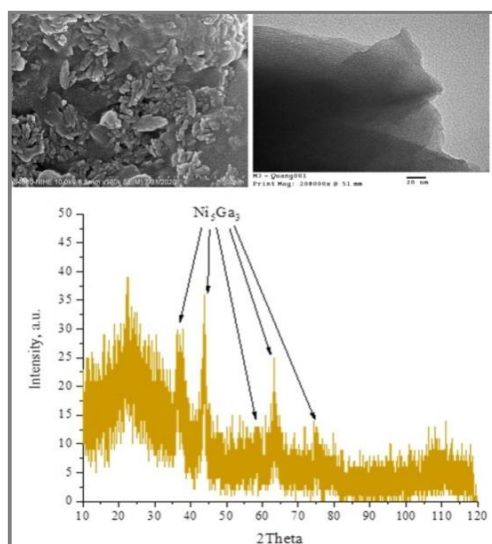
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### ABSTRACT

Advanced NiGaCu supported on ordered mesoporous silicon oxide (NiGaCu/MSO) catalyst with high activity and selectivity in conversion of CO<sub>2</sub> to CH<sub>3</sub>OH was prepared and characterized by SAXRD, WAXRD, SEM, TEM and BET. The characterizations showed that the catalyst possessed ordered mesoporous structure, focus pore width distribution high specific surface area and Ni<sub>5</sub>Ga<sub>3</sub> active phase being partially isomorphous substituted by Cu site. The catalyst was highly suitable for the conversion of CO<sub>2</sub> to CH<sub>3</sub>OH at relatively low pressure at 35 bar with high activity and selectivity. The conversion of CO<sub>2</sub> to CH<sub>3</sub>OH was fully investigated for optimizing the process's parameters. GC coupled with TCD and FID were used for determining the gas composition of the feedstock and generated products in the process.

### Graphical Abstract



SAXRD pattern of NiGaCu/MSO catalyst.

**Keywords:** Mesoporous materials, Carbon dioxide to methanol, Mesoporous silica, Cu based catalyst, Ni-Ga based catalyst.

## INTRODUCTION

Methanol was considered as one of the most important feedstock in the near future for chemistry industry [1, 2]. Methanol economy terminology declared by Olah [1] was predicted for its robust development after finding a good and cheap way to produce methanol.

Beside syngas, CO<sub>2</sub> was considered as a better feedstock for producing methanol because of its availability, sustainability and environmentally friendly. However, converting CO<sub>2</sub> to methanol required hard conditions and high activity catalysts because it was very stable under mild treatments [1, 2]. A set of Cu/ZnO based catalysts was applied as they were once used in the past and present in the conversion of syngas to methanol [3-5], but many disadvantages appeared; for example, the process required high to extreme pressure of CO<sub>2</sub> and H<sub>2</sub> [6]; there were competitions of other reactions generating by-products such as CO, CH<sub>4</sub> and coke; etc.

Ni-Ga based catalysts, which were recently developed, could be an excellent candidate to overcome those drawbacks. Many Ni-Ga based catalysis systems were developed including Ni-Ga neat alloy, Ni-Ga alloys supported on metal or non-metal oxides, and it was to say that the Ni<sub>5</sub>Ga<sub>3</sub> crystal phase played crucial role in the conversion of CO<sub>2</sub> to methanol under mild pressure [7, 8]. However, the Ni<sub>5</sub>Ga<sub>3</sub> could be active very differently upon different states; for example, the highly distributed and small particles of the Ni<sub>5</sub>Ga<sub>3</sub> could be much higher activity in the conversion of CO<sub>2</sub> to methanol, but the large block and agglomerated Ni<sub>5</sub>Ga<sub>3</sub> showed no effect on this process [7, 8].

On the other hand, by establishing many studies over these type of catalyst, we also found that the promoting metals could be very important in stabilizing and enhancing the catalysis activity and selectivity in the CO<sub>2</sub> conversion [9, 10]. One of our recent published reports related to preparations a set of NiGa, NiGaCo and NiGaCu based catalysts with variety of the distribution, metal promoter and support for the Ni<sub>5</sub>Ga<sub>3</sub> active sites. The NiGaCu supported on ordered mesoporous silicon oxide (NiGaCu/MSO) catalyst was the latest candidate exhibiting its very high activity and selectivity even under a relative low pressure. However, many investigations on the conversion of CO<sub>2</sub> to methanol need to be conducted over this process, and this paper published those investigations.

## MATERIALS AND METHODS

**Chemicals and feedstock:** Pure chemicals were ordered from Sigma Aldrich including Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ga(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, NaOH, Na<sub>2</sub>CO<sub>3</sub>, NaBH<sub>4</sub>, TEOS (Tetraethyl Orthosilicate), C<sub>2</sub>H<sub>5</sub>OH and CTAB (Cetyltrimethylammonium Bromide). Distilled water was produced in LASANY LPH-4 machine. H<sub>2</sub> and CO<sub>2</sub> gases met technical grades for the investigations.

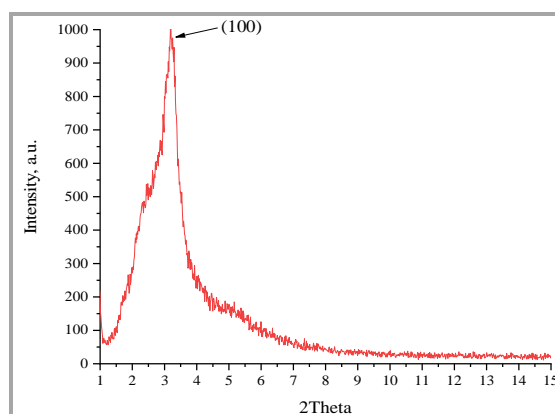
**Catalysis preparation:** The NiGaCu/MSO catalyst was prepared through impregnation method, and the process was described in reports elsewhere [9, 10]. The catalyst required an activation step by being reduced NaBH<sub>4</sub>/C<sub>2</sub>H<sub>5</sub>OH solution, in which the metal cations were mostly converted to the metal states.

**Investigation process:** The investigations on conversion of CO<sub>2</sub> to CH<sub>3</sub>OH over the NiGaCu/MSO were established using a micro-reactor system from Altamira AMI-200. One of the process was conducted by differencing the investigative pressures while other parameters were constant including temperature of 240°C, CO<sub>2</sub>/H<sub>2</sub> volume ratio of 1/3, total gas flow of 100 mL min<sup>-1</sup>, and volume space velocity of 6000 h<sup>-1</sup>. On the other hand, other investigations such as time (catalysis active life also), temperature, feedstock composition and gas flow were also studied by the same method. These variants included: pressures from 5 bars to 40 bars, CO<sub>2</sub>/H<sub>2</sub> volume ratios from 0.5/1.0 to 5.0/1.0, gas flows from 20 ml/min to 200 ml/min, and temperature from 150°C to 510°C. The gas compositions were determined by using TCD and FID coupled in Agilent 7890A gas chromatography machine from Thermo Finnigan Trace GC Ultra.

**Characterization and analysis:** XRD patterns were recorded on D8 Advance Bruker; SEM and TEM photos were captured on S-4800 NIHE and JEOL 1100, respectively; BET was measured on MicroActive for TriStar II Plus 2.03; GC-TCD-FID analysis was conducted on Thermo Finnigan Trace GC Ultra.

## RESULTS AND DISCUSSION

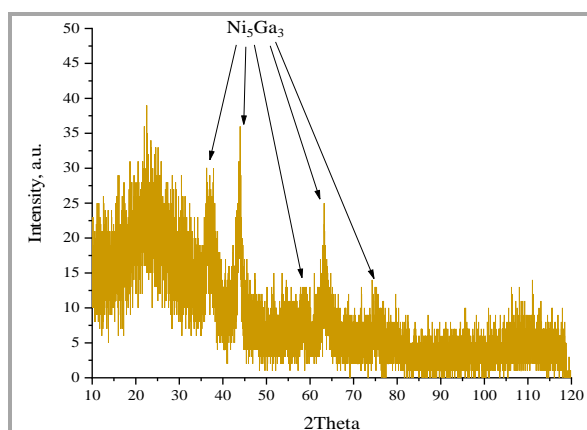
**XRD measurements:** XRD patterns of the NiGaCu/MSO catalyst were recorded by two techniques - small and wide angle (SAXRD and WAXRD, respectively), for determining its mesoporous and crystalline structures. The SAXRD pattern of the catalyst was plotted in figure 1.



**Figure 1.** SAXRD pattern of NiGaCu/MSO catalyst.

The SAXRD pattern clearly confirmed the ordered mesoporous structure of the catalyst when exposing fingerprint peak at  $2\theta = 3.1^\circ$  representing the (100) plane [11-13]. There was no further small angle peak assigned for hexagonal channels of the MSO support [9, 10] illustrating a less order structure of the catalyst. However, the fingerprint peak exhibited a high intensity showing that there was high density of the ordered mesoporous structure existing in the catalyst.

The decrease of order degree in the catalyst compared to the MSO support could be easily understandable because of the introduction of Ni, Ga and Cu sites into the mesoporous support. These sites could be diffused on to the pores, connected to the support's sites, and the mesoporous structure could be partially distorted because of these interactions. However, the ordered structure mainly remained proving the stability of the support during the impregnation and catalysis after-treatments.



**Figure 2.** SAXRD pattern of NiGaCu/MSO catalyst.

Along with the ordered mesoporous structure, the crystalline structure of the catalyst was also important for its activity in the conversion of CO<sub>2</sub> to CH<sub>3</sub>OH. WAXRD technique was applied to characterize this property. The WAXRD pattern was showed in [figure 2](#).

The results exhibited a set of peaks representing the Ni<sub>5</sub>Ga<sub>3</sub> active crystalline phase over a high background of the amorphous substance. These peaks located at 2θ = 38.6°, 43.7°, 58.0° and 64.0° all belonging to the Ni<sub>5</sub>Ga<sub>3</sub> crystal. No other crystalline peak was detected [7-10] proving that the existence of the Ni<sub>5</sub>Ga<sub>3</sub> active site along with the MSO amorphous support was the main composition of the NiGaCu catalyst. The signals of Cu derived phases were not detected; then it could conclude that the Cu site was isomorphically substituted in the Ni<sub>5</sub>Ga<sub>3</sub> site. The occurrence of the Ni<sub>5</sub>Ga<sub>3</sub> site distributing over the MSO support provided the catalyst with excellent diffusion and stability during the high temperature processes. The isomorphic substitution of the Cu in to the Ni<sub>5</sub>Ga<sub>3</sub> site also supported the catalyst with its stability and activity because the Cu and Ga sites were considered as the promoters of the catalyst.

**BET analysis:** BET surface of the NiGaCu/MSO catalyst was about 641.83 m<sup>2</sup> g<sup>-1</sup>, with a typical mesoporous structure isotherm revealing a hysteresis loop at medium high relative pressure [14-16]. Figure 3 exhibited this result and observation.

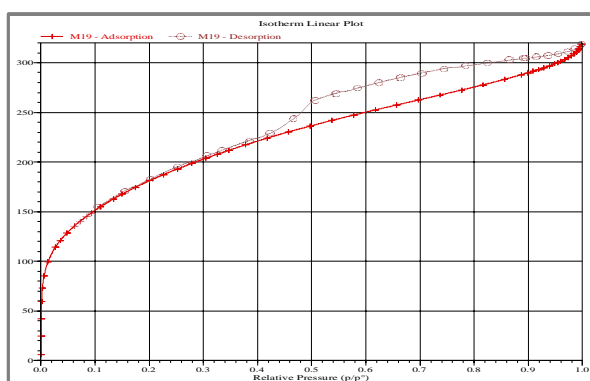


Figure 3. BET isotherm of NiGaCu/MSO catalyst.

Compared to other metal supported catalyst, the BET surface area of the NiGaCu/MSO catalyst was much higher because of the extreme high surface area of the MSO (up to about 1450 m<sup>2</sup> g<sup>-1</sup>) [5-11, 24-29]. The doping of Ni, Ga and Cu sites onto the MSO surface drastically decreased its surface area because these sites distributed over mainly internal into the mesoporous channels.

The pore width distribution of the NiGaCu/MSO catalyst was also studied by applying BJH technique. The BJH distribution curve was plotted in [figure 4](#).

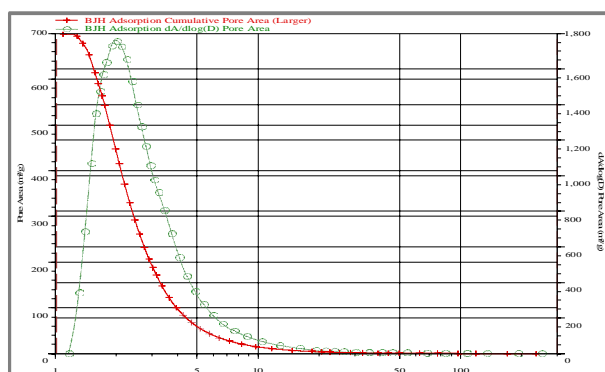
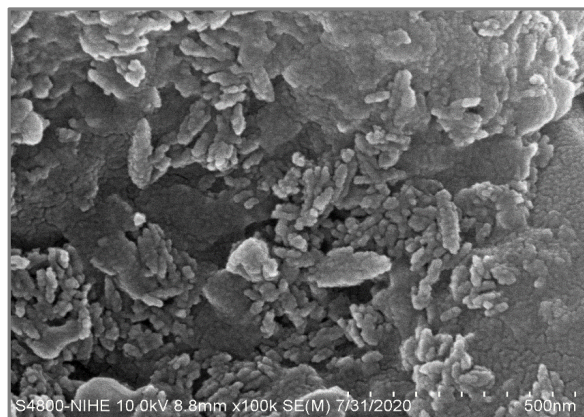


Figure 4. BJH pore distribution of NiGaCu/MSO catalyst.

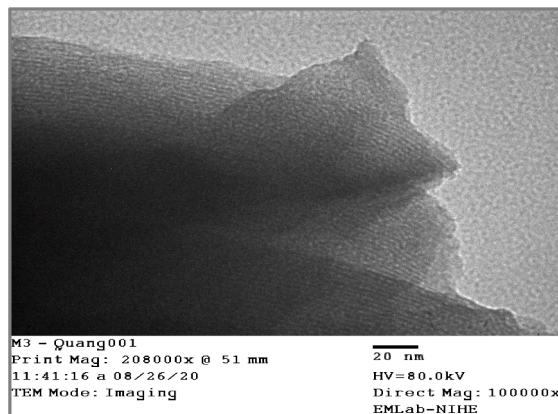
Observation and analysis clearly exhibited the mesoporous channels occurred inside the catalyst with concentrated porewidth of about 22 Å (2.2 nm) which was closed to the lower limit of the mesopores. It was reasonable with the relatively high 2theta of the mesoporous fingerprint peak [9, 10], and it was also reasonable with fine distribution of the Ni<sub>5</sub>Ga<sub>3</sub> sites inside the internal mesopores. The porewidth distribution was highly concentrated also corresponding to the high density of the ordered mesoporous structure of the catalyst as proved through SAXRD.

The evidence in the elsewhere data [9, 10] for the focus porewidth of the MSO at about 28 Å also confirmed the decrease of the porewidth after introducing Ni, Ga and Cu sites into the MSO support.

**SEM and TEM:** SEM and TEM images of the NiGaCu/MSO catalyst were given in figure 5 and 6.



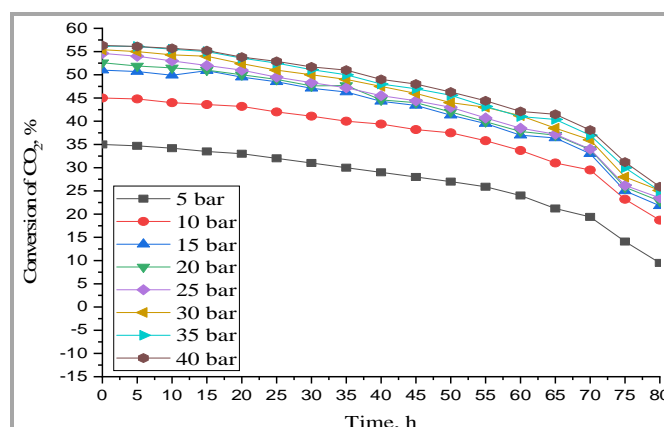
**Figure 5.** SEM image of NiGaCu/MSO catalyst.



**Figure 6.** TEM image of NiGaCu/MSO catalyst.

The SEM image exhibited a worm-like particle having sizes ranging from 10 nm to 30 nm. These particles contained the ordered mesoporous channels inside as being revealed in the TEM image. This structure was very typical in many mesoporous materials and was direct evidence proving the existence of the ordered mesoporous structure [9, 10].

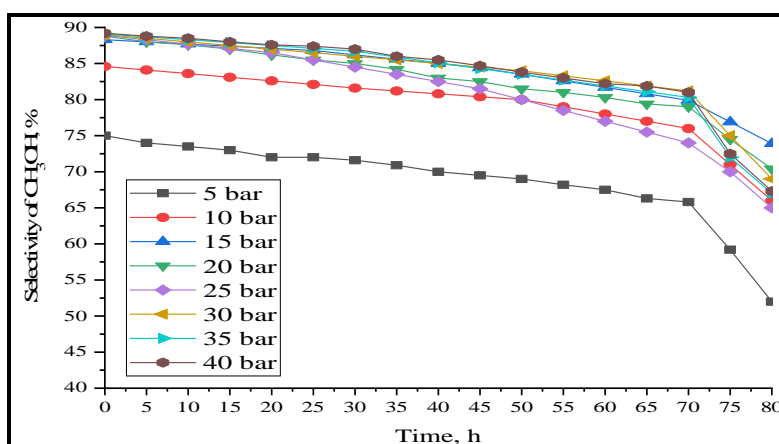
**Investigation on conversion of CO<sub>2</sub> to CH<sub>3</sub>OH over NiGaCu/MSO catalyst:** Effect of pressure on catalyst activity was conducted, and the results were collected and plotted in figure 7 and 8 and corresponding table 1 and 2, representing the conversion of CO<sub>2</sub> and the selectivity of CH<sub>3</sub>OH, respectively.



**Figure 7.** Conversion of CO<sub>2</sub> over NiGaCu/MSO catalyst at different pressures.

**Table 1.** Conversion of CO<sub>2</sub> over NiGaCu/MSO catalyst at different pressures

Time, h	Conversion of CO <sub>2</sub> at different pressures, %							
	5 bar	10 bar	15 bar	20 bar	25 bar	30 bar	35 bar	40 bar
0	35	45	51	52.6	54.6	55.4	<b>56.2</b>	56.3
5	34.7	44.8	50.7	51.9	54	55	<b>56.1</b>	56.1
10	34.2	44	49.9	51.5	53	54.3	<b>55.5</b>	55.7
15	33.5	43.6	50.9	51	52	54	<b>55</b>	55.2
20	33	43.2	49.5	50	51	52.4	<b>53.6</b>	53.8
25	32	42	48.5	49	49.5	51	<b>52.5</b>	52.9
30	31	41.1	47.1	47.6	48.3	50	<b>51.1</b>	51.7
35	30	40	46.3	47.7	47.2	49	<b>50</b>	51
40	29	39.4	44.3	44.6	45.5	47.5	<b>48</b>	49
45	28	38.2	43.4	44	44.4	46	<b>47</b>	48
50	27	37.5	41.3	42	43	44	<b>45.6</b>	46.3
55	25.9	35.8	39.5	39.9	40.7	43	<b>43.2</b>	44.4
60	24	33.7	37	37.8	38.5	41.2	<b>41</b>	42.1
65	21.2	31	36.4	37	37.2	38.5	<b>40.4</b>	41.5
70	19.4	29.5	33	33.9	34	36	<b>37</b>	38.1
75	14.1	23.2	25	25.8	26.2	28	<b>30</b>	31.2
80	9.5	18.7	21.8	22.8	23.5	25.1	<b>25</b>	25.9



**Figure 8.** Selectivity of CH<sub>3</sub>OH over NiGaCu/MSO catalyst at different pressures.

**Table 2.** Selectivity of CH<sub>3</sub>OH over NiGaCu/MSO catalyst at different pressures

Time, h	Selectivity of CH <sub>3</sub> OH at different pressures, %							
	5 bar	10 bar	15 bar	20 bar	25 bar	30 bar	35 bar	40 bar
0	75	84.6	88.3	88.8	88.9	89	<b>89.1</b>	89.2
5	74	84.1	88	88	88.3	88.5	<b>88.7</b>	88.8
10	73.5	83.6	87.7	87.6	87.7	88	<b>88.3</b>	88.5
15	73	83.1	87.4	87	87.1	87.5	<b>87.9</b>	88
20	72	82.6	87.1	86.2	86.5	87	<b>87.5</b>	87.6
25	72	82.1	86.8	85.5	85.5	86.5	<b>87.1</b>	87.4
30	71.6	81.6	86.2	85	84.5	86	<b>86.7</b>	87
35	70.9	81.2	85.6	84.2	83.5	85.5	<b>85.9</b>	86
40	70	80.8	85	83	82.5	85	<b>85.1</b>	85.5
45	69.5	80.4	84.4	82.5	81.5	84.5	<b>84.3</b>	84.7
50	69	80	83.5	81.5	80	84	<b>83.5</b>	83.8
55	68.2	79	82.6	81	78.5	83.3	<b>82.7</b>	83
60	67.5	78	81.7	80.3	77	82.6	<b>81.9</b>	82.2
65	66.3	77	80.8	79.4	75.5	81.9	<b>81.1</b>	81.9
70	65.8	76	79.9	79	74	81.2	<b>80.3</b>	81
75	59.2	71	76.9	74.5	70	75	<b>72</b>	72.5
80	52	66	73.9	70.4	65	69	<b>67</b>	67.3



Typically, the pressure and temperature mostly affected the conversion of CO<sub>2</sub> and the selectivity of CH<sub>3</sub>OH. Main reactions in the conversion of CO<sub>2</sub> to CH<sub>3</sub>OH [24, 25] were volume decrease in nature, so a relatively high pressure could accelerate the reaction speed and shifted the reactive balance to the right side (generating CO<sub>2</sub>).



The highest conversion of CO<sub>2</sub> and the highest selectivity of CH<sub>3</sub>OH could be achieved at 35 bar after the investigation of pressures, and they were 56.2% and 89.1%, respectively; namely the CH<sub>3</sub>OH yield reached its highest value of 50.07%. At 40 bar, these value only changed a very little value demonstrating the 35 bar pressure was the best value for this investigation. Compared to other catalysts published previously [9, 10, 12] including NiGa/MSO and NiGaCo/MSO, the NiGaCu/MSO catalyst clearly showed the much higher conversion of CO<sub>2</sub> and selectivity of CH<sub>3</sub>OH under the same pressures of 35 bar. Therefore, the process was investigated at pressure of 35 bar for the following studies.

One of the most impressive results obtained from these investigations was that the conversion of CO<sub>2</sub> and selectivity of CH<sub>3</sub>OH under 15 bar, reaching at 51.0% and 88.3%, respectively, were both considerably high compared to other researches [9, 10, 12]. The yield of CH<sub>3</sub>OH in this conditions was 45.03% noticeably corresponding to the one obtained from the investigations over the NiGaCo/MSO catalyst under 35 bar [10]. That was to say the NiGaCu/MSO catalyst could be highly active under low pressure compared to the traditional and modern catalysts for the CH<sub>3</sub>OH production.

Effect of temperature on catalyst activity was also conducted, and the results were collected and plotted in figure 9 and 10 and table 3 and 4, representing the conversion of CO<sub>2</sub> and the selectivity of CH<sub>3</sub>OH, respectively.

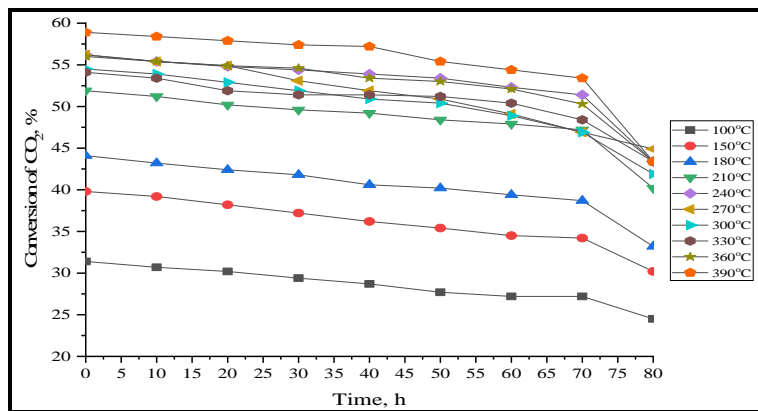


Figure 9. Conversion of CO<sub>2</sub> over NiGaCu/MSO catalyst at different temperatures.

Table 3. Conversion of CO<sub>2</sub> over NiGaCu/MSO catalyst at different temperatures

Time, h	Conversion of CO <sub>2</sub> at different temperatures, %									
	100	150	180	210	240	270	300	330	360	390
0	31.4	39.8	44.1	51.9	<b>56.2</b>	56.2	54.5	54.1	56	58.9
10	30.7	39.2	43.2	51.2	<b>55.4</b>	55.4	53.9	53.4	55.4	58.4
20	30.2	38.2	42.4	50.2	<b>54.8</b>	54.9	52.9	51.9	54.9	57.9
30	29.4	37.2	41.8	49.6	<b>54.4</b>	53.1	51.9	51.4	54.6	57.4
40	28.7	36.2	40.6	49.2	<b>53.9</b>	51.9	50.9	51.4	53.4	57.2
50	27.7	35.4	40.2	48.4	<b>53.4</b>	50.9	50.4	51.2	53	55.4
60	27.2	34.5	39.4	47.9	<b>52.3</b>	49.1	48.9	50.4	52.1	54.4
70	27.2	34.2	38.7	47.2	<b>51.4</b>	46.9	46.9	48.4	50.3	53.4
80	24.5	30.2	33.2	40.2	<b>43.4</b>	44.9	41.9	43.4	43.4	43.4

Results obtained from the conversion of CO<sub>2</sub> due to temperatures showed these values having an increase from 100°C to 240°C, a flat status from 240°C to 270°C, a decrease from 270°C to 330°C, and an increase again from 330°C to 390°C. The main reaction (1) was slightly exothermic causing the changes of the CO<sub>2</sub> conversion from 100°C to 330°C because the reaction required a high enough temperature for speeding up its velocity; however, when the temperatures became too high from the suitable temperature of 240°C, the balance of the reaction shifted to the reversed side yielding the decreases in the CO<sub>2</sub> conversion from 240°C to 330°C. From 330°C to 390°C, the process became complexed because of many other side reactions (reactions (2), (3) and (4)) [1, 2, 9, 10, 12] yielding the increase of CO<sub>2</sub> conversions but the decrease in the selectivity of the main product.

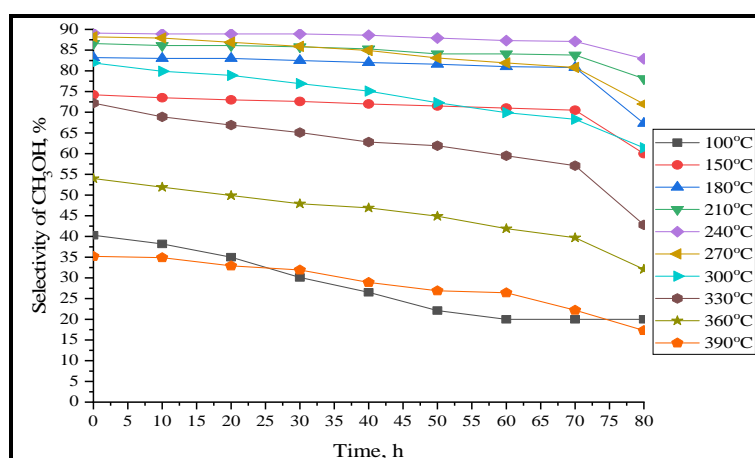
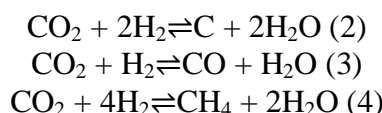


Figure 10. Selectivity of CH<sub>3</sub>OH over NiGaCu/MSO catalyst at different temperatures.

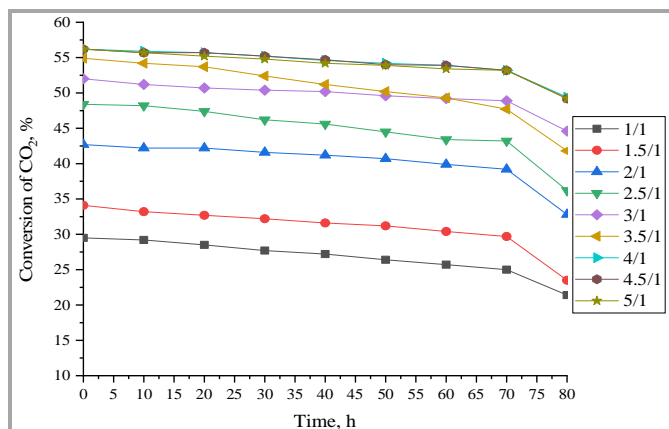
Table 4. Selectivity of CH<sub>3</sub>OH over NiGaCu/MSO catalyst at different temperatures

Time, h	Selectivity of CH <sub>3</sub> OH at different temperatures, %									
	100	150	180	210	240	270	300	330	360	390
0	40.3	74.2	83.2	86.6	<b>89.1</b>	88.2	81.9	72.2	54	35.2
10	38.2	73.5	83	86.1	<b>88.9</b>	87.9	79.9	68.9	51.9	34.9
20	35	73	83	86.1	<b>88.9</b>	86.9	78.9	66.9	49.9	32.9
30	30.1	72.6	82.5	85.8	<b>88.9</b>	85.9	76.9	65.1	47.9	31.9
40	26.5	72	82	85.3	<b>88.6</b>	84.9	75.1	62.8	46.9	28.9
50	22.1	71.5	81.6	84.1	<b>87.9</b>	83.1	72.3	61.9	44.9	26.9
60	20	71	81	84.1	<b>87.3</b>	81.9	69.9	59.5	41.9	26.4
70	20	70.5	80.8	83.8	<b>87.1</b>	80.8	68.3	57.1	39.7	22.2
80	20	60	67.3	78.1	<b>82.9</b>	72	61.4	42.8	32.1	17.3

Results obtained from these investigations also confirmed the competition of the side reactions after 330°C when the selectivity of CH<sub>3</sub>OH sharply decreased after this temperature. The decrease in the CH<sub>3</sub>OH selectivity from 240°C to 330°C also proved the exothermic property of the main reaction. Effect of temperature on the conversion of CO<sub>2</sub> and selectivity of CH<sub>3</sub>OH showing that a suitable temperature of 240°C could be applied to this process. At this temperature, the conversion of CO<sub>2</sub> and selectivity of CH<sub>3</sub>OH were both high, and the yield of CH<sub>3</sub>OH was maximized. The highest conversion of CO<sub>2</sub>, selectivity of CH<sub>3</sub>OH and CH<sub>3</sub>OH yield were 56.2%, 89.1% and 50.1%.



Effect of H<sub>2</sub>/CO<sub>2</sub> volume ratios on catalyst activity was also conducted, and the results were collected and plotted in figure 11 and 12, and table 5 and 6, representing the conversion of CO<sub>2</sub> and the selectivity of CH<sub>3</sub>OH, respectively.

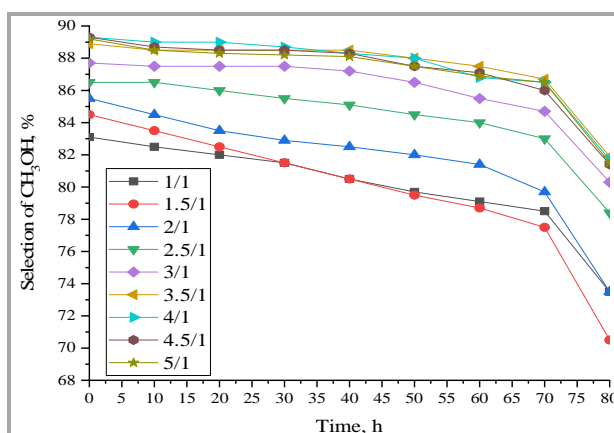


**Figure 11.** Conversion of CO<sub>2</sub> over NiGaCu/MSO catalyst at different H<sub>2</sub>/CO<sub>2</sub> volume ratios

**Table 5.** Conversion of CO<sub>2</sub> over NiGaCu/MSO catalyst at different H<sub>2</sub>/CO<sub>2</sub> volume ratios

Time h	Conversion of CO <sub>2</sub> at different H <sub>2</sub> /CO <sub>2</sub> volume ratios								
	1/1	1.5/1	2/1	2.5/1	3/1	3.5/1	4/1	4.5/1	5/1
0	29.5	34.1	42.7	48.4	52	54.9	56.2	56.2	56.2
10	29.2	33.2	42.2	48.2	51.2	54.2	55.9	55.7	55.7
20	28.5	32.7	42.2	47.4	50.7	53.7	55.7	55.7	55.2
30	27.7	32.2	41.6	46.2	50.4	52.4	55.2	55.2	54.8
40	27.2	31.6	41.2	45.6	50.2	51.2	54.6	54.7	54.2
50	26.4	31.2	40.7	44.5	49.6	50.2	54.2	54	53.9
60	25.7	30.4	39.9	43.4	49.2	49.3	53.9	53.9	53.4
70	25	29.7	39.2	43.2	48.9	47.7	53.2	53.2	53.2
80	21.4	23.5	32.8	36.2	44.6	41.8	49.4	49.2	49.2

The conversion of CO<sub>2</sub> gradually developed from the low to high H<sub>2</sub>/CO<sub>2</sub> volume ratios proving that the main reaction was positively affected by increasing them. This was caused by the volume reducing characteristic of the main reaction [9, 10]. The best H<sub>2</sub>/CO<sub>2</sub> volume ratio of 4/1 was chosen because the higher one did not raise the conversion.



**Figure 12.** Selectivity of CH<sub>3</sub>OH over NiGaCu/MSO catalyst at different H<sub>2</sub>/CO<sub>2</sub> volume ratios

**Table 6.** Selectivity of CH<sub>3</sub>OH over NiGaCu/MSO catalyst at different H<sub>2</sub>/CO<sub>2</sub> volume ratios

Time h	Selectivity of CH <sub>3</sub> OH at different H <sub>2</sub> /CO <sub>2</sub> volume ratios								
	1/1	1.5/1	2/1	2.5/1	3/1	3.5/1	4/1	4.5/1	5/1
0	83.1	84.5	85.5	86.5	87.7	88.9	<b>89.3</b>	89.3	89.2
10	82.5	83.5	84.5	86.5	87.5	88.5	<b>89</b>	88.7	88.5
20	82	82.5	83.5	86	87.5	88.5	<b>89</b>	88.5	88.3
30	81.5	81.5	82.9	85.5	87.5	88.5	<b>88.7</b>	88.5	88.2
40	80.5	80.5	82.5	85.1	87.2	88.5	<b>88.3</b>	88.3	88.1
50	79.7	79.5	82	84.5	86.5	88	<b>88</b>	87.5	87.5
60	79.1	78.7	81.4	84	85.5	87.5	<b>86.8</b>	87.1	86.9
70	78.5	77.5	79.7	83	84.7	86.7	<b>86.5</b>	86	86.5
80	73.5	70.5	73.5	78.4	80.3	81.9	<b>81.7</b>	81.4	81.5

The same conclusion came after the investigations of the CH<sub>3</sub>OH selectivity due to the H<sub>2</sub>/CO<sub>2</sub> volume ratios; then the best H<sub>2</sub>/CO<sub>2</sub> volume ratio of 4/1 was chosen. There was no reason to raise this ratio to a higher level because there was no evidence for the increase of either conversion of CO<sub>2</sub> or selectivity of CH<sub>3</sub>OH. It was to say at parameters of 35 bar, 240°C and H<sub>2</sub>/CO<sub>2</sub> volume ratio of 4/1, the catalyst activity could be stable up to 70 h. The highest conversion of CO<sub>2</sub> and selectivity of CH<sub>3</sub>OH also reached at 56.2% and 89.3%, respectively. The highest yield of CH<sub>3</sub>OH, therefore, could reach 50.2%. These results clearly exhibited high catalysis activity compared to most of the other researches [6, 17-19].

On the whole, the conversion of CO<sub>2</sub> and the selectivity of CH<sub>3</sub>OH decreased by time during all the investigations. However, over many analyzed results, they drastically reduced after about 70 h of the reactions corresponding to the life time of the catalyst was about 70 h in continuous operation. After this time, the catalyst should be replaced by a new batch, and the spent catalyst should be regenerated. Some reasons could be assigned for the sharp decrease of the catalyst activity after 70 h of process: nanoscale coke clusters deposited on the catalysis active sites; the active sites were partially sintered under high temperature for a long time; the active sites were oxidized by adjacent oxygen atoms [1, 9].

## APPLICATION

The NiGaCu/MSO catalyst could be applied in conversion of CO<sub>2</sub> to CH<sub>3</sub>OH in one-staged process under mild pressure. The catalyst could be considered for replacing other traditional Cu/Al/Zn based catalysts.

## CONCLUSION

NiGaCu/MSO was characterized for its ordered mesoporous structure, high specific surface area of 641.83 m<sup>2</sup>/g, concentrated and small mesoporous pore width of 22 Å. The Ni<sub>5</sub>Ga<sub>3</sub> active phase was distributed over the MSO support, and Cu site was isomorphic substituted into the active phase framework. Investigations on effect of many parameters to the conversion of CO<sub>2</sub> to CH<sub>3</sub>OH were fully conducted. The results showed that the process should be established at temperature of 240°C, pressure of 35 bar, H<sub>2</sub>/CO<sub>2</sub> volume ratio of 4/1, and the catalyst could be active after 70 h of the process. The highest conversion of CO<sub>2</sub> and selectivity of CH<sub>3</sub>OH reached 56.2% and 89.3% respectively, under these conditions. The highest yield of CH<sub>3</sub>OH could reach 50.2%.

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