



## Methanol Production from Carbon Dioxide over Ordered Mesoporous NiGaCu Based Catalyst in Low Pressure Process

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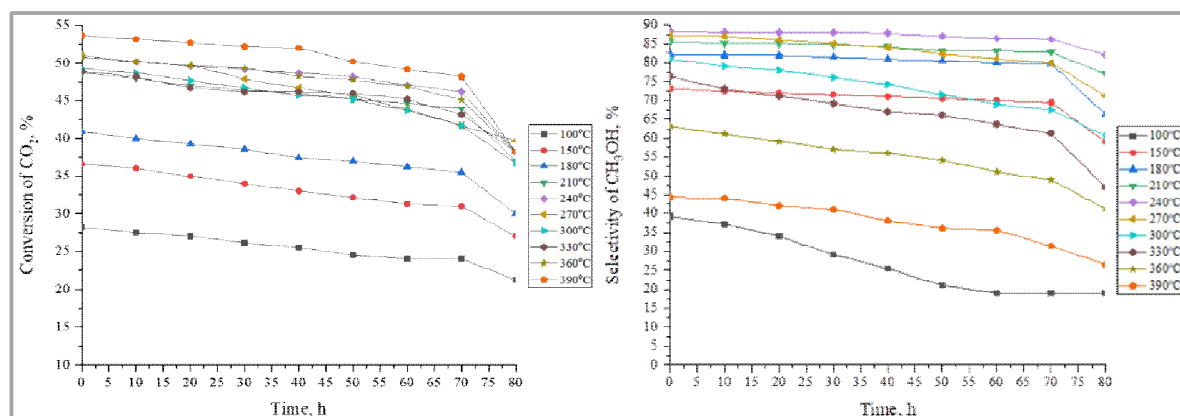
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### ABSTRACT

This study covered characterizations of NiGaCu supported on mesoporous silica oxide (NiGaCu/MSO) catalyst for its ordered mesoporous structure and its state of the active sites, and the NiGaCu/MSO catalyst was applied in CO<sub>2</sub> to CH<sub>3</sub>OH reduction process. Many parameters were investigated in the process, and the results showed that the process could be established under low pressure of 15 bar. Under this pressure, the catalyst activity was still very high leading to the CH<sub>3</sub>OH yield of about 45%. Some techniques were applied in this study including XRD, EDX, XPS and GC-TCD-FID.

### Graphical Abstract



Conversion of CO<sub>2</sub> and selectivity of CH<sub>3</sub>OH over NiGaCu/MSO catalyst

**Keywords:** CO<sub>2</sub> conversion, promoter, copper based catalyst, Ni-Ga based catalyst.

### INTRODUCTION

NiGa based catalysts recently received great attention because of their excellent potentials in the conversion of CO<sub>2</sub> to CH<sub>3</sub>OH – one of the most important process heading to the Methanol Economy in the future [1, 4, 5, 14-19]. Some publications reported preparations of different types of Ni-Ga

based catalysts [2-10, 12], and others implied their deep studies on understanding how the Ni-Ga based catalysts showed high activity and selectivity, even under relatively low pressures [9, 10, 12, 20, 21]. The most important results obtained from these researches were to find the main active site of the whole process – the Ni<sub>5</sub>Ga<sub>3</sub> alloyed crystal [4, 5]. However, there would be difficult for the Ni<sub>5</sub>Ga<sub>3</sub> to expose all of its potentials in the CH<sub>3</sub>OH production. Some major disadvantages: the site was too easy to be sintered; the sites required high and stable surface area for enhancing its distribution; the sites could be easily coagulated under high temperature.

Some developments were published to overcome these drawbacks; for example, loading the Ni<sub>5</sub>Ga<sub>3</sub> to a high surface area material such as the ordered mesoporous material, introducing promoting metals into the active site to stabilizing its active state during the process [9, 10, 12, 20]. Recently, our latest and novel NiGaCu/MSO catalyst was developed by both introducing Cu to the Ni<sub>5</sub>Ga<sub>3</sub> site and distributing the sites into the MSO support [20]. However, the role of the MSO support and the promoting Cu metal were not fully understandable. In this study, these gaps would be filled by applying a series of techniques including XRD, EDX and XPS for determining the state of the active site in the catalyst; then full investigations of the CO<sub>2</sub> to CH<sub>3</sub>OH conversion over the NiGaCu/MSO catalyst was also conducted.

## MATERIALS AND METHODS

**Chemicals and feedstock:** Chemicals using in the study included nickel nitrate (II) hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), gallium (II) nitrate nonahydrate (Ga(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), copper (II) nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O), sodium hydroxide (NaOH), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), sodium borotetrahydride (NaBH<sub>4</sub>), tetraethyl orthosilicate (TEOS), anhydrous ethanol (C<sub>2</sub>H<sub>5</sub>OH) and cetyltrimethylammonium (CTAB) all ordered from Sigma Aldrich with high grade purity for synthesis. Distilled water was produced using LASANY LPH-4. Gas feedstocks including H<sub>2</sub> and CO<sub>2</sub> were domestically ordered for the investigations.

**Preparation and characterizations of NiGaCu/MSO catalyst:** The preparation of the NiGaCu/MSO catalyst were reported elsewhere [20] through impregnation wetness process. The process progressed through the impregnation of Ni, Ga and Cu precursors over the MSO support; drying and calcination of the NiGaCu/MSO precipitation in high temperature; conversion of cation mixtures in the calcined precipitation to active alloy states under NaBH<sub>4</sub>/ethanol solution. The structure of the NiGaCu/MSO catalyst was characterized by techniques such as XRD, EDX and XPS in D8 Advance Bruker, JED-2300 Analysis Station, and Kratos Supra employing a monochromated Al K $\alpha$  X-ray source (h $\nu$  = 1486.7 eV), respectively.

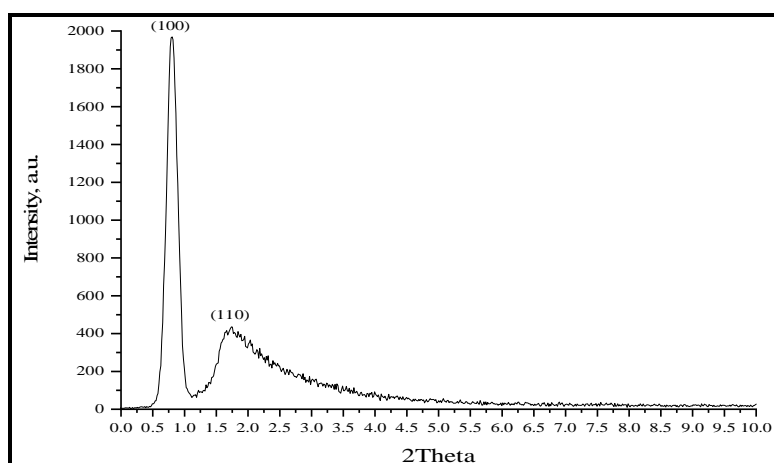
**Investigation of CO<sub>2</sub> conversion to CH<sub>3</sub>OH over NiGaCu/MSO catalyst:** The investigations were conducted at low pressure of 15 bar because other pressures were investigated in another paper [20]. The process was also conducted in Altamira AMI-200 micro-reaction system for continuous procedure.

Effects of temperature, CO<sub>2</sub>/H<sub>2</sub> gas volume ratio, hour volume space velocity (HVSV) and reaction time were systematically investigated at values of 150°C - 510°C, 0.5/1.0 - 5.0/1.0, 1000 h<sup>-1</sup> - 8000 h<sup>-1</sup>, and 0 h - 80 h, respectively. The conversion of CO<sub>2</sub> and the selectivity of CH<sub>3</sub>OH were determined from the gas compositions analyzed by GC-TCD-FID method in Agilent 7890A, Thermo Finnigan Trace GC Ultra.

## RESULTS AND DISCUSSION

**Characterizations of NiGaCu/MSO catalyst:** Investigations on the catalyst preparation and its characterizations including SEM, TEM, BET, H<sub>2</sub>-TPR, were reported in elsewhere publication [20]. In this study, the structure and properties of the catalyst including XRD, EDX and XPS were conducted for illustrating the isomorphic substitution of Cu into the Ni<sub>5</sub>Ga<sub>3</sub> active phase. Ordered

mesoporous structure of the NiGaCu/MSO catalyst was characterized by SAXRD (Small Angle X-Ray Diffraction). [Figure 1](#) exhibited the pattern.

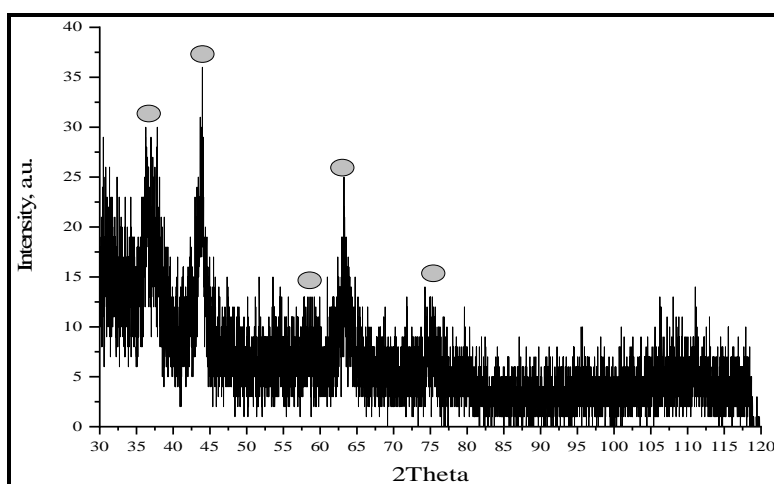


**Figure 1.** SAXRD pattern of NiGaCu/MSO catalyst

The pattern obtained from the SAXRD result of the NiGaCu/MSO catalyst exhibited a fingerprint peak assigned for (100) plane and a side peak for (110) plane, representing a hexagonal like mesoporous structure. The high intensity of these two peaks also confirmed a high density of the ordered mesoporous structure in the catalyst [9-13]. These peaks also had the same profile with many similar peaks observed from other typical mesoporous materials such as MCM-41 or SBA-15 [12, 13]. That was to say there was no major effect happened after introducing Ni, Ga and Cu into the MSO support, even under high temperature of the post-treatment of the catalysis preparation.

There was no major change in the ordered mesoporous structure after the catalysis preparation because the pore walls of the MSO support possessed excellent thermal and physiochemical stability. The hexagonal structure, the high specific surface area and the concentrated pore width of the ordered mesoporous system in the catalyst were also clearly demonstrated in the mentioned publication [20].

The WAXRD (Wide Angle X-Ray Diffraction) pattern of the NiGaCu/MSO catalyst was exhibited in [figure 2](#), showing its crystalline and amorphous components.



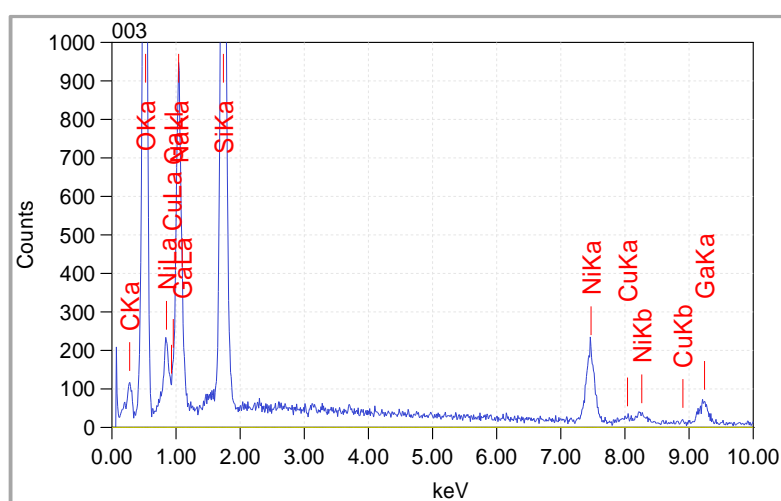
**Figure 2.** SAXRD pattern of NiGaCu/MSO catalyst.

WAXRD pattern of the NiGaCu/MSO catalyst only showed specific peaks corresponding to the  $\text{Ni}_5\text{Ga}_3$  active alloyed crystals at  $2\theta$  values =  $36.9^\circ$ ,  $43.9^\circ$ ,  $58.8^\circ$ ,  $63.2^\circ$  and  $75.4^\circ$  [4, 5, 10, 12, 20]. There

was no evidence for the existence of any copper based crystalline phase [7-10] yielding to two possible cases: Cu was isomorphically substituted into the Ni<sub>5</sub>Ga<sub>3</sub> alloyed phase by replacing Ni or Ga position; Cu located over the MSO support in amorphous phase of oxides. The former one had higher possibility than the latter because Cu<sup>2+</sup> was definitely easier to be reduced to the metallic state than the Ni<sup>2+</sup> and Ga<sup>3+</sup>, which were almost converted to the metallic state under the reduction solution (NaBH<sub>4</sub>/ethanol). Besides, in the former case, Cu sites, as a promoter, played a crucial role in strengthening the catalysis performance in the CO<sub>2</sub> conversion because, as proved by many studies [14-19], Cu was one of the best metal for the process.

The results obtained from the SAXRD, WAXRD and other publication [20] strongly proved that the active phase of the CO<sub>2</sub> to CH<sub>3</sub>OH conversion was highly distributed over the MSO support with ordered and stable mesoporous structure. These conditions probably enhanced the conversion of CO<sub>2</sub> to CH<sub>3</sub>OH as being demonstrated in this study.

Elemental composition of the catalyst was also analyzed by EDX method. Figure 3 and table 1 revealed this result.



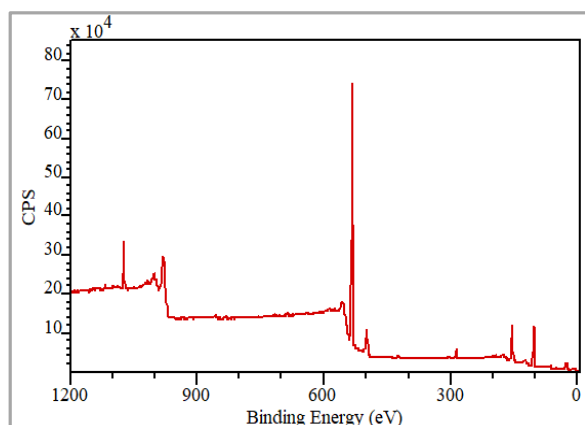
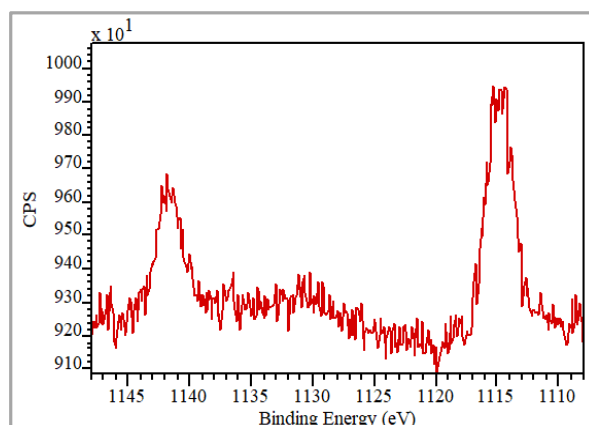
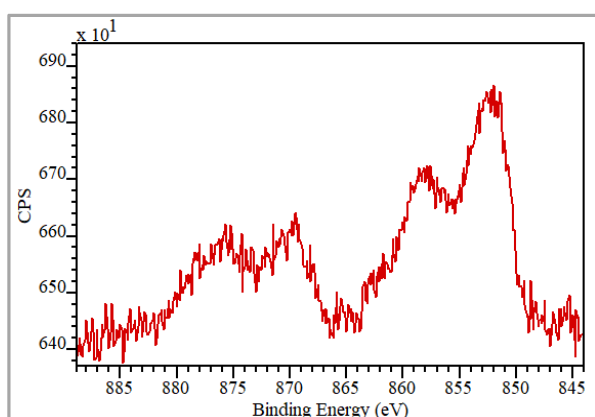
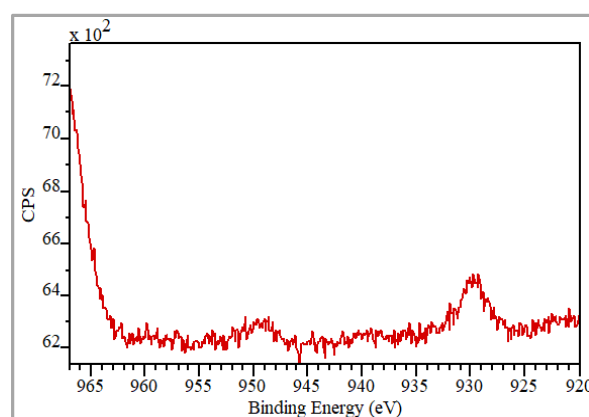
**Figure 3.** EDX spectrum of NiGaCu/MSO catalyst

**Table 1.** Elemental composition of NiGaCu/MSO catalyst

Elements	C	O	Si	Na	Ni	Cu	Ga	Total
Molar composition, %	2.30	60.73	28.83	3.26	3.08	0.13	1.67	100.00

EDX spectrum observed from the figure 3 showed that there were C, O, Si, Na, Ni, Cu and Ga (H could not be detected by EDX method, but its content was always very small compared to others), and analysis extracted from these spectra also showed them, respectively representing to precursors or feedstock of the catalysis preparation such as C in CO<sub>3</sub><sup>2-</sup>, O in all types, Si in MSO support, Na<sup>+</sup> in carbonate, Ni, Cu and Ga in nitrate salts.

Molar ratio of Ni/Ga/Cu corresponded to 3.08/1.67/0.13 being much closed to 5.00/2.71/0.22, respectively. It revealed that the Ni/(Ga+Cu) volume ratio equaled to 5/2.93 being very closed to the molar ratio of Ni/Ga in the Ni<sub>5</sub>Ga<sub>3</sub> active phase. Combined with the results obtained from the XRD method that was a high potential for an isomorphous substitution of Cu into the Ni<sub>5</sub>Ga<sub>3</sub> active site where the Ga sites were partially replaced by the Cu ones. Confirmation on the isomorphous substitution could be reached considering the XPS method. The total XPS spectrum was plotted in figure 4, and its Cu, Ni, Ga elemental spectrum were also plotted in figure 5 to 8.

**Figure 4.** XPS spectrum of NiGaCu/MSO catalyst**Figure 5.** XPS spectrum of Ga<sub>2p</sub> site in NiGaCu/MSO catalyst**Figure 6.** XPS spectrum of Ni<sub>2p</sub> site in NiGaCu/MSO catalyst.**Figure 7.** XPS spectrum of Cu<sub>2p</sub> site in NiGaCu/MSO catalyst

Signals obtained from the XPS spectrum of Ga<sub>2p</sub> orbital at bond energies of 1115.0 eV and 1142.0 eV confirmed its metallic state [10]. There was no peak representing Ga<sub>2</sub>O<sub>3</sub> or any other oxides illustrating that the Ga<sup>3+</sup> sites were totally reduced under the reduction procedure [10]. Combined with the XRD and EDX from the previous results, it was to conclude all Ga sites were transferred into the Ni<sub>5</sub>Ga<sub>3</sub> active sites.

Signals obtained from the XPS spectrum of Ni<sub>2p</sub> orbital at bond energies of 851.6 eV, 858.2 eV, 869.4 eV and 875.9 eV corresponded to some states such as metallic Ni in alloy state with Ga, metallic Ni, metallic Ni in alloy state with Cu and metallic Ni in connection with the MSO support through oxygen bridge [10]. There was also no peak representing to oxides of Ni proving that all Ni<sup>2+</sup> sites were reduced to metallic Ni sites in the Ni<sub>5</sub>Ga<sub>3</sub> active sites.

Similarly, signals obtained from the XPS spectrum of Cu<sub>2p</sub> orbital at bond energies of 929.7 eV and 951.1 eV also exhibited metallic Cu in alloy state with Ga, and Ni [15-17]. There was also no peak representing to oxides of Cu proving that all Cu<sup>2+</sup> sites were reduced to metallic Cu sites in connection with Ni and Ga sites. There were also peak of Cu<sub>LMM</sub> orbital at energy of 552.4 eV that also belonged to metallic Cu state [15-17]. It was strong evidence, along with other characterizations such as XRD and EDX, to confirm that Cu was isomorphic substituted into the Ni<sub>5</sub>Ga<sub>3</sub> sites. According to EDX results, the active site now could be assigned as Ni<sub>5</sub>Ga<sub>2.71</sub>Cu<sub>0.22</sub>.

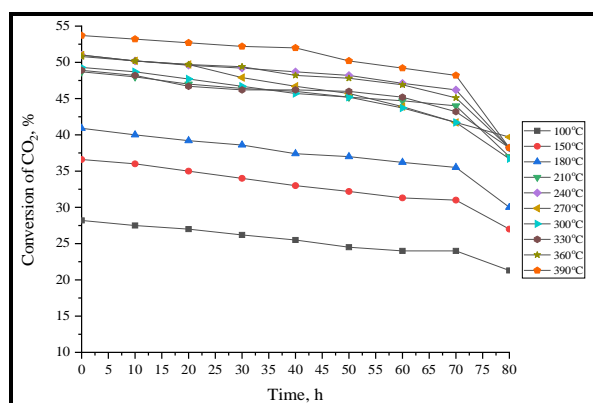
On the whole, the characterizations for the NiGaCu/MSO catalyst in this study strongly confirmed its hexagonal ordered mesoporous structure, the partially isomorphic substitution of Cu for

Ga in the Ni<sub>5</sub>Ga<sub>3</sub> sites, and new active sites of Ni<sub>5</sub>Ga<sub>2.71</sub>Cu<sub>0.22</sub>. This kind of NiGaCu/MSO catalyst was applied in the investigation of CO<sub>2</sub> conversion to CH<sub>3</sub>OH.

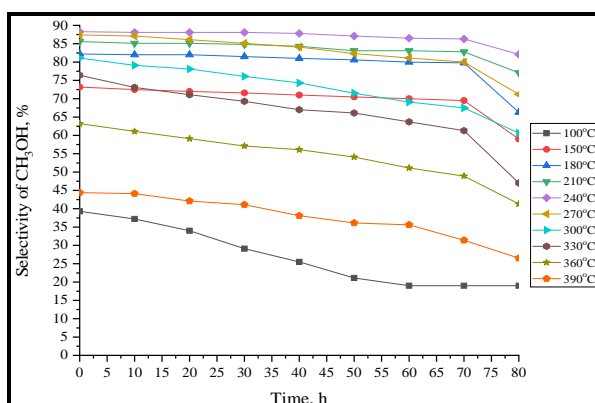
**Effect of paramaters on conversion of CO<sub>2</sub> to CH<sub>3</sub>OH over NiGaCu/MSO catalyst:** As mentioned above, the effect of pressure was investigated in the other study [20], and it showed the values of 56.2% and 89.1% for the conversion of CO<sub>2</sub> and the selectivity of CH<sub>3</sub>OH at 35 bar, respectively. The CH<sub>3</sub>OH yield, therefore, reached its highest value of 50.07%. However, one of the most outstanding investigation was obtained under 15 bar when the conversion of CO<sub>2</sub> and the selectivity of CH<sub>3</sub>OH reached 51.0% and 88.3%, respectively. It could be concluded that, in the conversion process over the NiGaCu/MSO catalyst, the pressure could be sharply decreased from 35 bar to 15 bar, but the conversion of CO<sub>2</sub> and the selectivity of CH<sub>3</sub>OH were slightly reduced. That was to say the NiGaCu/MSO catalyst could be highly active even at low pressure of 15 bar.

There were many reasons could be assigned for its high activity at lower pressure: the MSO support possessed high specific surface area [9, 10, 12] providing the active sites an excellent distribution and stability; the isomorphic substitution of promoter Cu into the Ni<sub>5</sub>Ga<sub>3</sub> active sites could strengthen the active site stability at high temperature; introduction of Cu into the Ni<sub>5</sub>Ga<sub>3</sub> sites also enhanced the selectivity of Cu sites in generation of CH<sub>3</sub>OH from CO<sub>2</sub>; Ni and Ga had good adsorption capacity to CO that could reduce its generation as a side product. Therefore, pressure of 15 bar was chosen for all following investigations. All the targets of the investigations were to consider the conversion of CO<sub>2</sub> and the selectivity of CH<sub>3</sub>OH when varying the parameters.

Effects of different temperatures on the process performance were collected and plotted in figure 8 and 9.



**Figure 8.** Effect of temperature(at 15 bar) on conversion of CO<sub>2</sub>.

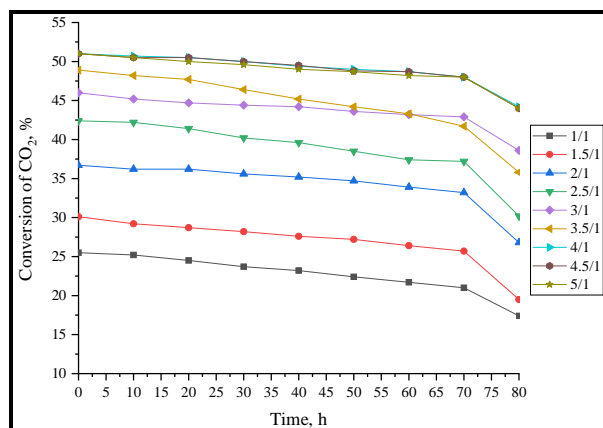


**Figure 9.** Effect of temperature on selectivity of CH<sub>3</sub>OH (at 15 bar).

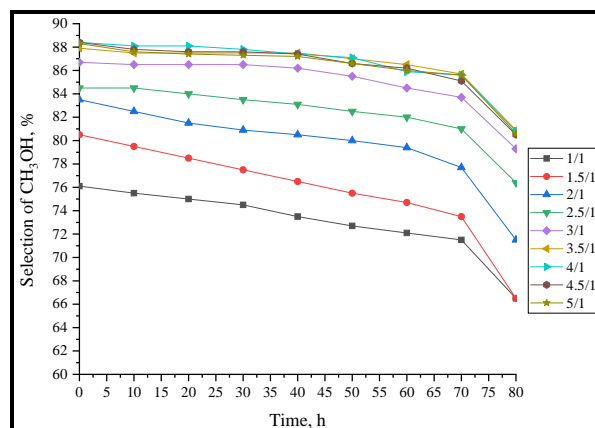
For the conversion of CO<sub>2</sub> in figure 8, observations pointed out that from 100°C to 210°C, it sharply increased; from 240°C to 390°C, it became stable and varied in a small amount. For the selectivity of CH<sub>3</sub>OH in figure 9, it clearly increased from 100°C to 240°C, and then it decreased at the higher temperature. **The highest selectivity of CH<sub>3</sub>OH reached 88.3% at 240°C, and at this temperature, the conversion of CO<sub>2</sub> reached 51.0%. The yield of CH<sub>3</sub>OH, therefore, reached 45.03%.**

Explanation for these trends could be obtained from the kinetic property of the main reaction - slightly exothermic reaction. The reaction required high enough temperature for speeding up the reaction velocity, but the too high temperature inhibited the right reaction. On the other hand, at very high temperature, many side reactions could be happened leading to decrease the selectivity of CH<sub>3</sub>OH even when the conversion of CO<sub>2</sub> still increased [20].

Effects of different H<sub>2</sub>/CO<sub>2</sub> volume ratios on the process performance were collected and plotted in figure 10 and 11.



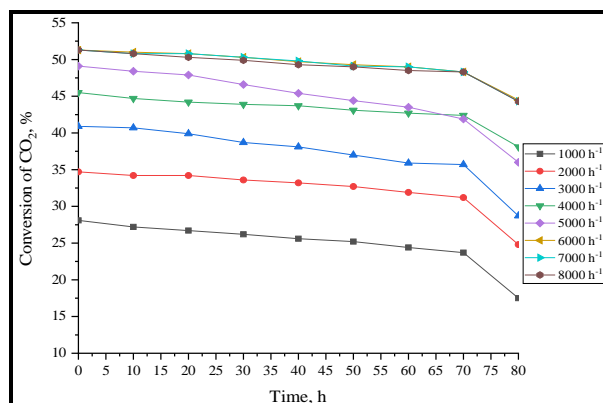
**Figure 10.** Effect of  $H_2/CO_2$  volume ratio on conversion of  $CO_2$  (at 15 bar).



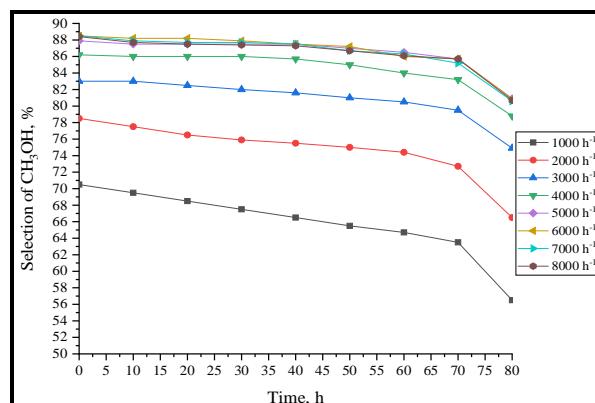
**Figure 11.** Effect of  $H_2/CO_2$  volume ratio on selectivity of  $CH_3OH$  (at 15 bar).

Results obtained from figure 10 showed a gradual increase in the conversion of  $CO_2$  by the increase of the  $H_2/CO_2$  volume ratio. However, the conversion (51.0%) became stable from the volume ratio of 4/1 to 5/1 because the process approached to its balance point [9, 10, 20]. There was similar trend in the selectivity of  $CH_3OH$  diagram where it reached the highest value of 88.4% at the volume ratio of 4/1. Therefore, the  $H_2/CO_2$  volume ratio of 4/1 was chosen for further investigations.

Effects of different values of the hour volume space velocity (HVSV) on the process performance were collected and plotted in figure 12 and 13.



**Figure 12.** Effect of HVSV on conversion of  $CO_2$



**Figure 13.** Effect of HVSV on selectivity of  $CH_3OH$ .

Results obtained from figure 12 also showed a gradual increase in the conversion of  $CO_2$  by the increase of HVSV, and the conversion of  $CO_2$  reached 51.3% at the HVSV of  $6000\text{ h}^{-1}$ ; then the conversion of  $CO_2$  became stable even when raising the HVSV to  $8000\text{ h}^{-1}$ . The increases of the  $CO_2$  conversion were caused by increasing the amount of total feedstock including  $H_2$  and  $CO_2$ ; this feedstock ran through the catalyst bed having constant volume, so there was more feedstock to be converted to the product over the catalyst bed. However, when the HVSV became too high, the catalyst capacity limited to a constant turnover frequency; therefore, the conversion of  $CO_2$  became stable. The similar trend was also observed to the selectivity of  $CH_3OH$  when the best selectivity reached 88.5% at the HVSV of  $6000\text{ h}^{-1}$ . Hence, the HVSV of  $6000\text{ h}^{-1}$  was chosen for this investigation.

On the whole, that was to say at parameters including *pressure of 15 bar, temperature of  $240^\circ C$ ,  $H_2/CO_2$  volume ratio of 4/1, HVSV of  $6000\text{ h}^{-1}$ , 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 could be at 51.3% and 88.5%, respectively, and the yield of CH<sub>3</sub>OH then would be 45.40%.** The life span of the catalyst could be considered at 70 h because the conversion of CO<sub>2</sub> and the selectivity of CH<sub>3</sub>OH sharply decreased after that; then, the catalyst should be regenerated for recycling. Some reasons could be assigned for the decrease in the catalyst activity including the formation of the deposited nanometer coke clusters, the sintering of the catalysis active sites, the oxidation of the active site, the modification of the active site to other forms [9, 10, 12, 20, 21].

## APPLICATION

The conversion of CO<sub>2</sub> to CH<sub>3</sub>OH over NiGaCo/MSO catalyst was applicable to a pilot scale, then it could be opened to larger scale to approach the production of CH<sub>3</sub>OH. This process was high potential because the pressure was sharply decreased compared to other traditional production of CH<sub>3</sub>OH.

## CONCLUSION

The NiGaCu/MSO catalyst possessed hexagonal ordered mesoporous structure, Ni<sub>5</sub>Ga<sub>2.71</sub>Cu<sub>0.22</sub> active sites formed by isomorphic substitution of Cu in to the former Ni<sub>5</sub>Ga<sub>3</sub> sites. The isomorphic substitution was fully illustrated by the XPS technique, and it provided catalyst with stable, high activity and selectivity properties in conversion of CO<sub>2</sub> to CH<sub>3</sub>OH.

The catalyst with the active site was applied in the CO<sub>2</sub> conversion under hydrogen. The investigations showed the best parameters for this process including pressure of 15 bar, temperature of 240°C, H<sub>2</sub>/CO<sub>2</sub> volume ratio of 4/1, HVSV of 6000 h<sup>-1</sup>. At these conditions, the highest conversion of CO<sub>2</sub>, the selectivity of CH<sub>3</sub>OH and the yield of CH<sub>3</sub>OH reached 51.3%, 88.5%, and 45.40%, respectively.

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