



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

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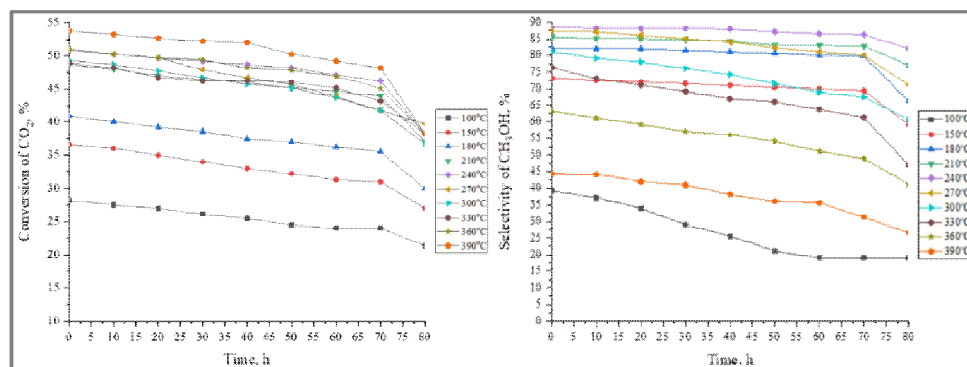
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ABSTRACT

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 CO₂ to CH₃OH 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 CH₃OH yield of about 45%. Some techniques were applied in this study including XRD, EDX, XPS and GC-TCD-FID.

Graphical Abstract



Conversion of CO₂ and selectivity of CH₃OH over NiGaCu/MSO catalyst.

Keywords: CO₂ 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 CO₂ to CH₃OH—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 Ni₅Ga₃ alloyed crystal [4, 5]. However, there would be difficult for the Ni₅Ga₃ to expose all of its potentials in the CH₃OH 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 Ni₅Ga₃ 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 Ni₅Ga₃ 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 a full investigation of the CO₂ to CH₃OH 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(NO₃)₂·6H₂O), gallium (II) nitrate nonahydrate (Ga(NO₃)₃·9H₂O), copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O), sodium hydroxide (NaOH), sodium carbonate (Na₂CO₃), sodium borotetrahydride (NaBH₄), tetraethyl orthosilicate (TEOS), anhydrous ethanol (C₂H₅OH) 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 H₂ and CO₂ 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 NaBH₄/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 α X-ray source (h ν = 1486.7 eV), respectively.

Investigation of CO₂ conversion to CH₃OH 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, CO₂/H₂ 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⁻¹ – 8000 h⁻¹, and 0 h–80 h, respectively. The conversion of CO₂ and the selectivity of CH₃OH 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, H₂-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 Ni₅Ga₃ active phase. Ordered

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

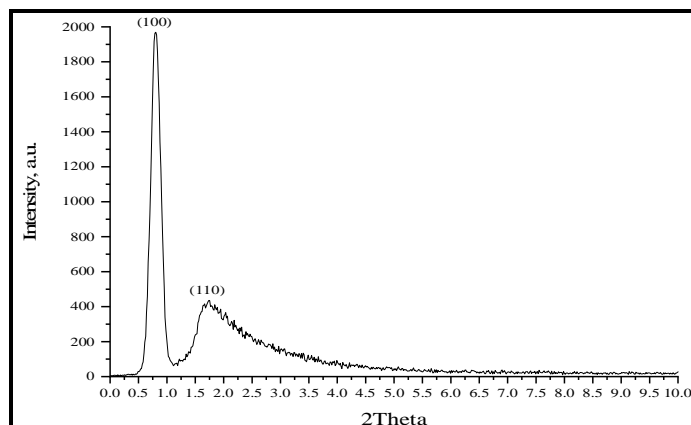


Figure 1. SAXRD pattern of NiGaCu/MSO catalyst.

The pattern obtained from the SAXRD result of the NiGaCu/MSO catalyst exhibited a finger print 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.

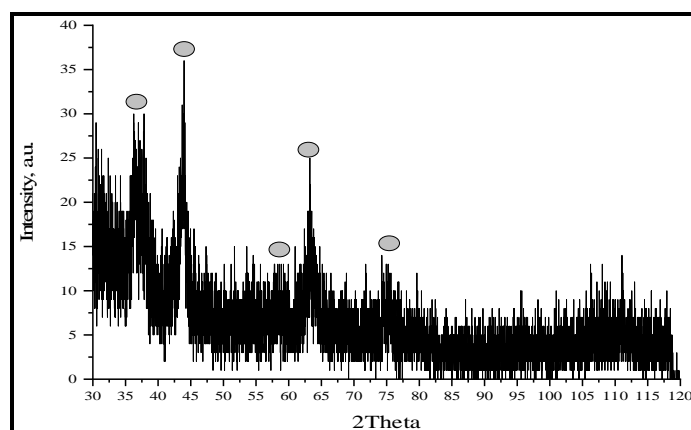


Figure 2. WAXRD pattern of NiGaCu/MSO catalyst.

WAXRD pattern of the NiGaCu/MSO catalyst only showed specific peaks corresponding to the Ni_5Ga_3 active alloyed crystals at 2θ values = 36.9° , 43.9° , 58.8° , 63.2° and 75.4° [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_5Ga_3 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^{2+} was definitely easier to be reduced to the metallic state than the Ni^{2+} and Ga^{3+} , which were almost converted to the metallic state under the reduction solution ($\text{NaBH}_4/\text{ethanol}$). Besides, in the former case, Cu sites, as a promoter, played a crucial role in strengthening the catalysis performance in the CO_2 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_2 to CH_3OH conversion was highly distributed over the MSO support with ordered and stable mesoporous structure. These conditions probably enhanced the conversion of CO_2 to CH_3OH 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.

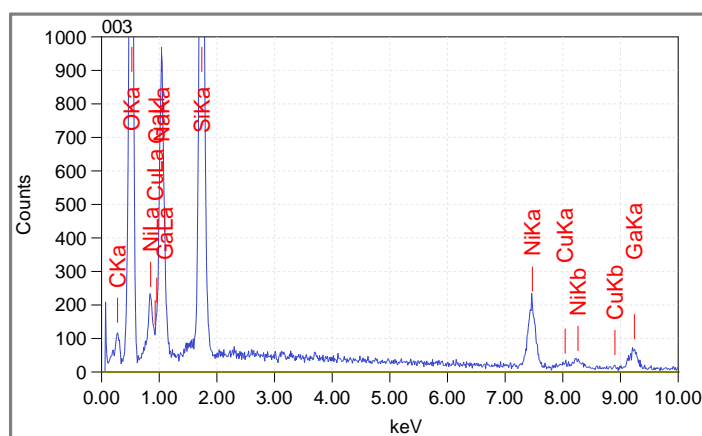


Figure 3. EDX spectrum of NiGaCu/MSO catalyst.

| Elements | C | O | Si | Na | Ni | Cu | Ga | Total |
|---------------------|------|-------|-------|------|------|------|------|--------|
| Molar Composition % | 2.30 | 60.73 | 28.83 | 3.26 | 30.8 | 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_3^{2-} , O in all types, Si in MSO support, Na^+ 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 $\text{Ni}/(\text{Ga}+\text{Cu})$ volume ratio equaled to 5/2.93 being very closed to the molar ratio of Ni/Ga in the Ni_5Ga_3 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_5Ga_3 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.

Signals obtained from the XPS spectrum of Ga_{2p} orbital at bond energies of 1115.0 eV and 1142.0 eV confirmed its metallic state [10]. There was no peak representing Ga_2O_3 or any other oxides illustrating that the Ga^{3+} 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 Ni₅Ga₃ active sites.

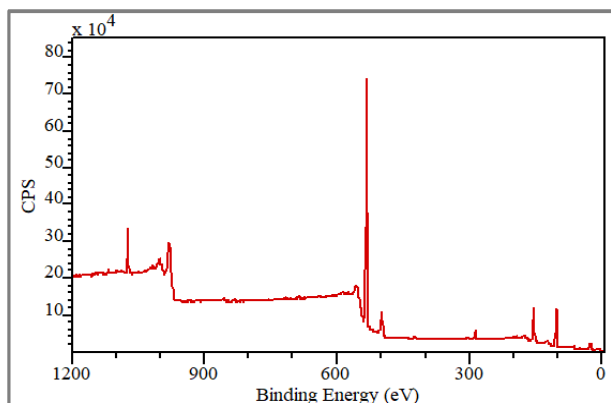


Figure 4. XPS spectrum of NiGaCu/MSO catalyst.

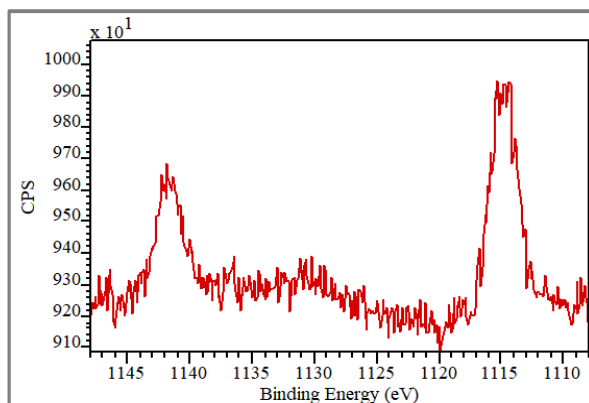


Figure 5. XPS spectrum of Ga_{2p} site in NiGaCu/MSO catalyst.

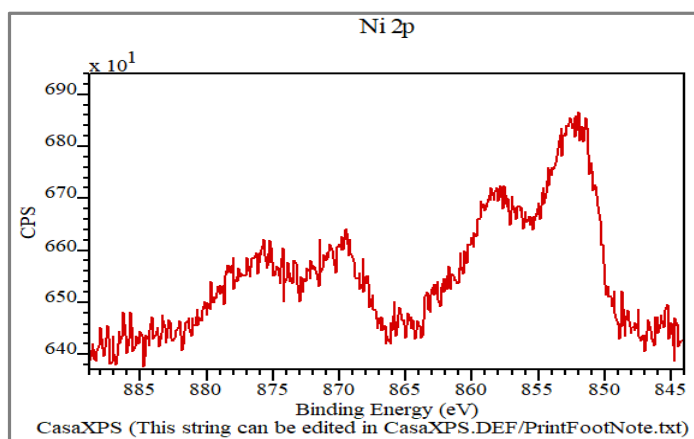


Figure 6. XPS spectrum of Ni_{2p} site in NiGaCu/MSO catalyst.

Signals obtained from the XPS spectrum of Ni_{2p} 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 Ni²⁺ sites were reduced to metallic Ni sites in the Ni₅Ga₃ active sites.

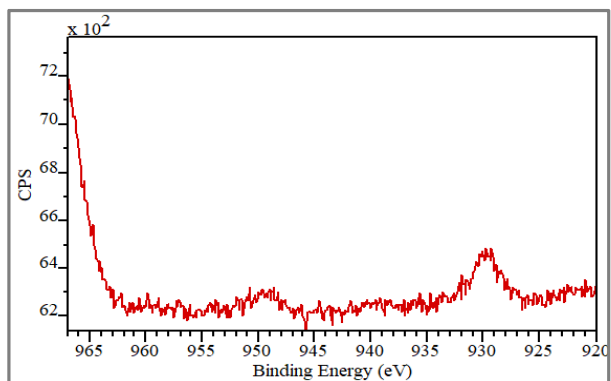


Figure 7a. XPS spectrum of Cu_{2p} site in NiGaCu/MSO catalyst.

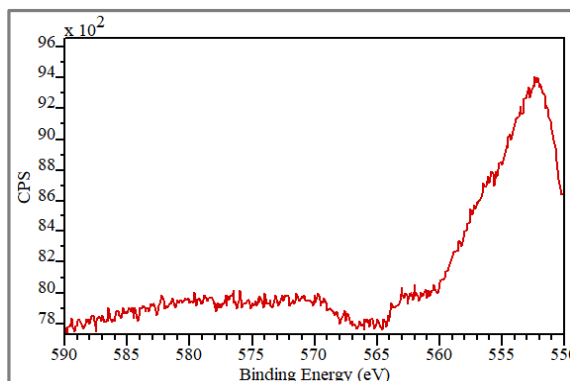


Figure 7b. XPS spectrum of Cu_{LMM} site in NiGaCu/MSO catalyst.

Similarly, signals obtained from the XPS spectrum of Cu_{2p} 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^{2+} sites were reduced to metallic Cu sites in connection with Ni and Ga sites. There was also peak of Cu_{LMM} 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 isomorphically substituted into the Ni_5Ga_3 sites. According to EDX results, the active site now could be assigned as $\text{Ni}_5\text{Ga}_{2.71}\text{Cu}_{0.22}$.

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_5Ga_3 sites, and new active sites of $\text{Ni}_5\text{Ga}_{2.71}\text{Cu}_{0.22}$. This kind of NiGaCu/MSO catalyst was applied in the investigation of CO_2 conversion to CH_3OH .

Effect of parameters on conversion of CO_2 to CH_3OH 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_2 and the selectivity of CH_3OH at 35 bar, respectively. The CH_3OH yield, therefore, reached its highest value of 50.07%. However, one of the most outstanding investigations was obtained under 15 bar when the conversion of CO_2 and the selectivity of CH_3OH 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_2 and the selectivity of CH_3OH 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_5Ga_3 active sites could strengthen the active site stability at high temperature; introduction of Cu into the Ni_5Ga_3 sites also enhanced the selectivity of Cu sites in generation of CH_3OH from CO_2 ; 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_2 and the selectivity of CH_3OH when varying the parameters.

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

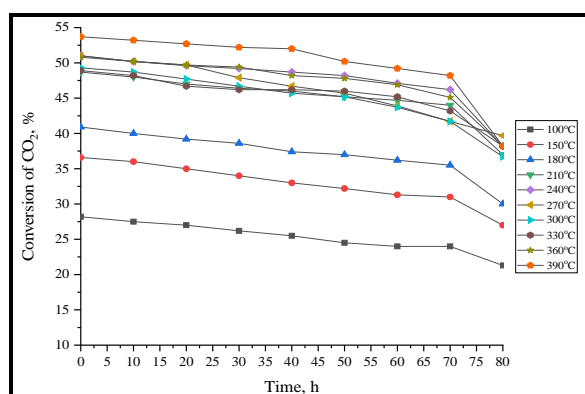


Figure 8. Effect of temperature (at 15 bar) on conversion of CO_2 .

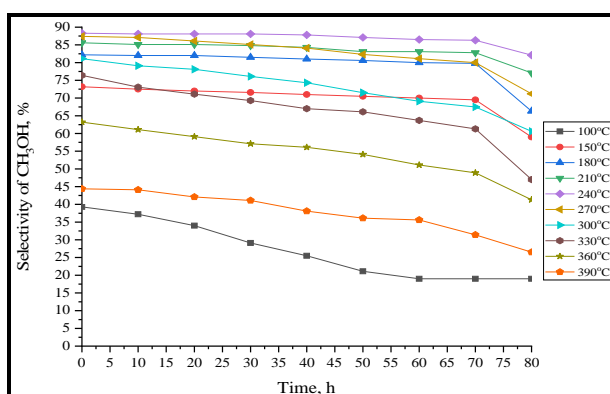


Figure 9. Effect of temperature on selectivity of CH_3OH (at 15 bar).

For the conversion of CO_2 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_3OH in figure 9, it clearly increased from 100°C to 240°C, and then it decreased at

the higher temperature. *The highest selectivity of CH₃OH reached 88.3% at 240 °C, and at this temperature, the conversion of CO₂ reached 51.0%. The yield of CH₃OH, 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 CH₃OH even when the conversion of CO₂ still increased [20].

Effects of different H₂/CO₂ volume ratios on the process performance were collected and plotted in figure 10 and 11.

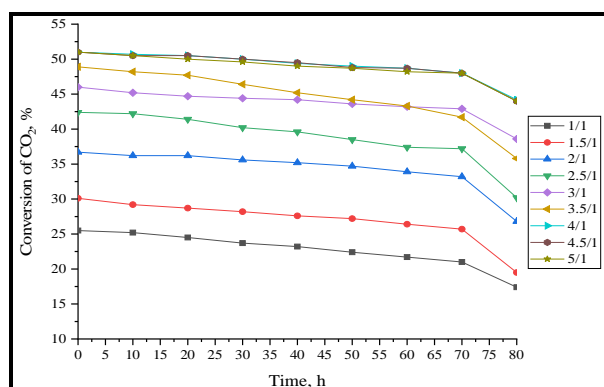


Figure 10. Effect of H₂/CO₂ volume ratio on conversion of CO₂ (at 15 bar).

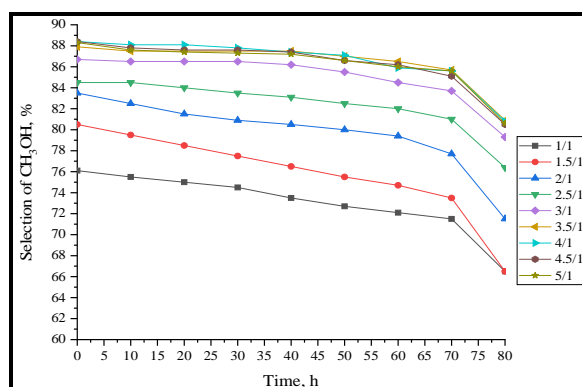


Figure 11. Effect of H₂/CO₂ volume ratio on selectivity of CH₃OH (at 15 bar).

Results obtained from Figure 10 showed a gradual increase in the conversion of CO₂ by the increase of the H₂/CO₂ 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 CH₃OH diagram where it reached the highest value of 88.4% at the volume ratio of 4/1. Therefore, the H₂/CO₂ 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.

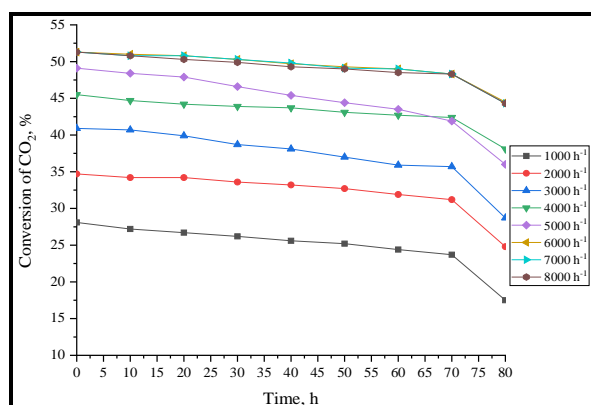


Figure 12. Effect of HVSV on conversion of CO₂.

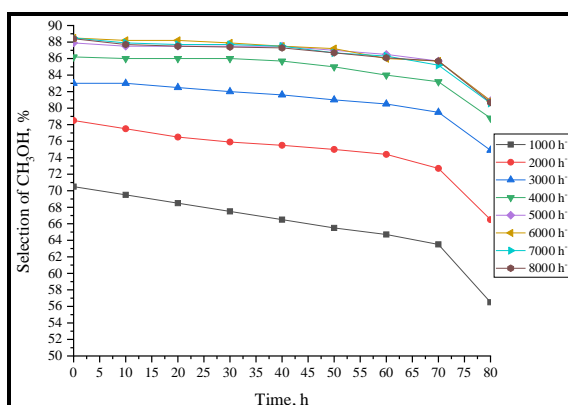


Figure 13. Effect of HVSV on selectivity of CH₃OH.

Results obtained from figure 12 also showed a gradual increase in the conversion of CO₂ by the increase of HVSV, and the conversion of CO₂ reached 51.3% at the HVSV of 6000 h⁻¹; then the

conversion of CO₂ became stable even when raising the HVSV to 8000 h⁻¹. The increases of the CO₂ conversion were caused by increasing the amount of total feedstock including H₂ and CO₂; 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 CO₂ became stable. The similar trend was also observed to the selectivity of CH₃OH when the best selectivity reached 88.5% at the HVSV of 6000 h⁻¹. Hence, the HVSV of 6000 h⁻¹ was chosen for this investigation.

On the whole, that was to say at parameters including *pressure of 15 bar, temperature of 240°C, H₂/CO₂ volume ratio of 4/1, HVSV of 6000 h⁻¹, the catalyst activity could be stable up to 70 h. The highest conversion of CO₂ and selectivity of CH₃OH could be at 51.3% and 88.5%, respectively, and the yield of CH₃OH then would be 45.40%. The life span of the catalyst could be considered at 70 h* because the conversion of CO₂ and the selectivity of CH₃OH 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 CO₂ to CH₃OH over NiGaCo/MSO catalyst was applicable to a pilot scale, and then it could be opened to larger scale to approach the production of CH₃OH. This process was high potential because the pressure was sharply decreased compared to other traditional production of CH₃OH.

CONCLUSION

The NiGaCu/MSO catalyst possessed hexagonal ordered mesoporous structure, Ni₅Ga_{2.71}Cu_{0.22} active sites formed by isomorphic substitution of Cu in to the former Ni₅Ga₃ 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 CO₂ to CH₃OH. The catalyst with the active site was applied in the CO₂ conversion under hydrogen. The investigations showed the best parameters for this process including pressure of 15 bar, temperature of 240°C, H₂/CO₂ volume ratio of 4/1, HVSV of 6000 h⁻¹. At these conditions, the highest conversion of CO₂, the selectivity.

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