eProceedings Chemistry 3 (2018) 126-133

eISSN 2550-1453 http://eproceedings.chemistry.utm.my/

Nanocrystalline of Ruthenium-Iron Promoted Alkaline Oxides Based Catalysts for CO_2/H_2 Methanation Reaction

Siti Rafinah Arjan and Susilawati Toemen*

Department of Chemistry, Faculty of Science, UniversitiTeknologi Malaysia, 81310 Johor Bahru, Malaysia
Corresponding Author: susilawatitoemen@kimia.fs.utm.my

Article history :
Received: 2 October June 2018
Accepted: 7 November 018

GRAPHICAL ABSTRACT

Catalysts prepared

ABSTRACT

New catalyst formulation of alkaline earths (M' = Mg, Ca, Sr and Ba) based catalysts had been successfully prepared in this research by doping with iron (Fe) and noble metal ruthenium (Ru) in the ratio of 5:10:85 supported on alumina via impregnation method. Two different ratios of catalyst Ru/Fe/M' (5:30:65)/Al_2O_3 and Ru/Fe/M' (5:10:85)/Al_2O_3 calcined at 1000°C had been prepared at the screening stage. The best catalyst from this stage was further investigated in optimization process at different calcination temperatures between 900 – 1100 ºC and loadings between 80 - 90 wt.%. An in-house-built micro reactor with Fourier transform infrared (FTIR) and TQ analysis software were used to study the percentage of CO_2 conversion and also the percentage of CH_4 formation. From the catalytic study, Ru/Fe/Sr (5:10:85)/Al_2O_3 catalyst calcined at 1000ºC was categorized as a promising catalyst which gave 90.1% CO_2 conversion and 100% selectivity of CH_4 at reaction temperature of 300 ºC. This catalyst showed a polycrystalline structure with a mixture of SrO, Al_2O_3, Fe_2O_3 and RuO_2 species which was obtained by an X-Ray diffraction (XRD) analysis. The characterization of surface morphology illustrated that the catalyst surface was covered with agglomerated and aggregated particles with staghorn coral shape. An energy dispersive X-Ray (EDX) analysis confirmed the presence Sr, Fe, Ru and Al on the catalyst surface. The analysis from thermogravimetry analysis (TGA) revealed that 1000 °C of calcination temperature was good enough to produce pure metal oxide for the catalysts.

Keywords: alkaline earth metal, impregnation method, calcination temperature

1. INTRODUCTION

Methanation of carbon dioxide has been studied over a number of metal oxide-based catalysts *e.g.* Ni, Mn, Ce and Zr) supported on various metal oxides *e.g.* Al_2O_3, SiO_2 and TiO_2. The most widely used catalyst is Ni based catalysts for CO_2 methanation due to the low cost, but this catalyst is very sensitive towards chemical attack due to the formation of cokes and working at high reaction temperature. To overcome this problem, researchers have explored the use of various inexpensive transition metals such as Mn, Ni, and Cu. Metal oxides are less active than metals, but they are stable in catalytic conditions [1]. In this work, alkaline earth metal oxides, Ru/Fe/M'–Al_2O_3 (M' = Mg, Ca, Sr and Ba) are chosen as based catalysts due to its low cost and high activity. In fact, alkaline earth metal oxides such as magnesium oxide (MgO), calcium oxide (CaO), strontium oxide (SrO) and barium oxide (BaO) are used because of their catalytic activities that are closely related to their surface basic strength. As atomic number increases, the cationic size increases and the polarizing power decreases, therefore the basicity increases. Generally, the sequence of the four catalysts according to their catalytic activities are MgO<CaO<SrO<BaO [2].

Currently, trimetallic catalysts have been given more attention in catalytic reaction. The approach of combining three metals as catalysts is to increase stability and the performance catalytic activity. However, only a few papers have reported on CO_2/H_2 methanation by trimetallic catalysts. Therefore, transition metal (Fe) was used as a dopant while noble metal (Ru) was used as co-dopant in Ru/Fe/M'–Al_2O_3 catalysts in this research, which can improve stability, achieve lower reaction temperature and tune the catalytic performance. The aim of this study is to screen the potential dopants and co-dopants of Fe and Ru over alumina supported alkaline earth metal oxides, Ru/Fe/M'–Al_2O_3 catalysts in CO_2 conversion. In this research, removal of CO_2 by using trimetallic Ru/Fe/M'–Al_2O_3 (M' = Mg, Ca, Sr and Ba) catalysts was investigated. Then for the most active catalyst, the influence of catalyst preparation parameters such as calcination temperature and alkaline earth metal loading in CO_2/H_2 methanation was evaluated using an in-house built micro reactor coupled with Fourier transform infrared (FTIR) in order to find the optimum conditions of catalyst preparation and the corresponding values of two major process parameters; calcination temperature and alkaline earth metal loading.

2. EXPERIMENTAL

The experiment was divided into three main stages. The first stage focused on preparation of catalysts. All the catalysts were prepared by the wet impregnation technique using nitrate and chloride salts as metal precursors. For the screening process, 5 g of based catalyst (M = Mg, Ca, Sr and Ba) were weighed in a beaker and then dissolved in a small amount approximately 10 mL of distilled water. The mixed catalyst solution was prepared by mixing an appropriate amount of dopant catalyst (Fe) and co-dopant catalyst (Ru) salt solutions with the based catalyst solution according to its ratio. A homogeneous mixture was obtained by electromagnetic stirring at room temperature for 15 minutes. Then, 10 g of alumina support were immersed into the mixed catalyst solution until the solution totally adsorbed on the surface of the alumina support. Next, the supported catalyst was transferred onto glass wool in evaporating dish and aged inside an oven at 80 – 90ºC for 24 hours to remove water and to allow good coating between the metal and support surface. It will be followed by calcination in the furnace at 1000 ºC for 5 hours using a ramp rate of 5ºC/min to eliminate water while nitrate and chloride ions were converted into catalysts. The preparation process was performed with two different ratios of catalyst which was (65:30:5) and (85:10:5) at 1000 ºC. The potential mixed catalyst was optimized by amount of based loading which was 60 wt.% and 70 wt.% and then further calcined separately at 900ºCand 1100ºC for 5 hours using same ramp rate of 5ºC/min. The same procedures were repeated for other catalysts. Finally, trimetallic catalysts were labelled $Ru/Fe/M/Al_2O_3$. Next is catalytic activity measurement. The catalytic activity measurements were analyzed by using two instrumental analyses which were Fourier transform infrared spectrometer (FTIR) and TQ analysis. The FTIR was used to determine the percentage of CO_2 while the TQ analysis was used to measure the formation of methane. All reactions were conducted under atmospheric pressure. Lastly, the potential catalysts were subjected to several characterization techniques to study the chemical and physical properties. The information obtained was highly useful to understand the relationship between the properties and its catalytic performance towards methanation formation. In this research, the characterization techniques that were used was thermogravimetry analysis (TGA), X-ray diffraction (XRD) and field emission scanning electron microscopy - energy dispersive X-ray (FESEM-EDX).

3. RESULTS AND DISCUSSION

3.1. Catalytic Screening

For catalytic screening, the loading of alkaline earth metal was fixed to 65%. Thus, the ratio for trimetallic catalyst was 5:30:65. Prior to the start of the testing, all the prepared catalysts were subjected to pretreatment at 300°C for 30 minutes in the presence of H_2. The reason for preheating the catalyst is to activate the catalyst as well as to remove the moisture in the catalyst. Table 1 shows the catalytic performance of alumina supported alkaline earth metal oxide-based catalysts with first row transition metal (Fe) as its dopant catalyst and noble metal (Ru) as its co-dopant catalyst. All the catalysts were calcined at 1000°C for 5 hours. According to the results in Table 1, Ru/Fe/Mg (5:30:65)/Al_2O_3 catalyst gave only 21.8% conversion of CO_2 with 15.1% formation of CH_4 even at a high reaction temperature of 300 °C. By changing alkaline earth metal, Mg to the Ca, it was slightly increased to 30.2% with 26.1% formation of CH_4 for Ru/Fe/Ca (5:30:65)/Al_2O_3 catalyst. Then conversion of CO_2 continues increasing for Ru/Fe/Sr (5:30:65)/Al_2O_3 catalyst with 54.6% and 51.8% formation of CH_4 while Ru/Fe/Ba (5:30:65)/Al_2O_3 catalyst gave 62.1% conversion of CO_2 with 59.1% formation of CH_4 at high reaction temperature of 300 °C. Lee *et al*. had reported that the alkaline earth metal act as Lewis acids to which water molecule coordinates via an oxygen atom, which induces polarity in the O-H bond. The resulting polarized H_2O molecule is very reactive and can attack CO to produce CO_2 and H_2. Therefore, the higher basicity of catalyst will give higher catalytic activity.

Table 1 Conversion of CO_2 over various alumina supported alkaline earth metal oxide-based catalysts calcined at 1000 °C for 5 hours

Alumina Supported catalyst	**Reaction temperature**					
	100°C		**200°C**		**300°C**	
	CO_2 (%)	**CH_4 (%)**	**CO_2 (%)**	**CH_4 (%)**	**CO_2 (%)**	**CH_4 (%)**
Ru/Fe/Mg (5:30:65)/Al_2O_3	3.2	1.27	7.78	6.53	21.8	15.1
Ru/Fe/Ca (5:30:65)/Al_2O_3	2.61	1.91	4.76	3.82	30.2	26.1
Ru/Fe/Sr (5:30:65)/Al_2O_3	1.17	0.63	6.62	5.94	54.6	51.8
Ru/Fe/Ba (5:30:65)/Al_2O_3	3.41	2.81	8.76	7.64	62.1	59.1

In order to increase the catalytic performance, the loading of alkaline earth metal was increased to 85%. Thus, the ratio for trimetallic catalyst was 5:10:85. According to the results in Table 2, Ru/Fe/Mg (5:30:65)/Al_2O_3 catalyst gave only 40.5% conversion of CO_2 with 35.1% formation of CH_4 even at a high reaction temperature of 300 °C. By changing alkaline earth metal, Mg to the Ca, it was slightly increased to 64.6% with 51.6% formation of CH_4 for Ru/Fe/Ca (5:30:65)/Al_2O_3 catalyst. Then conversion of CO_2 increased abruptly for Ru/Fe/Sr (5:30:65)/Al_2O_3 catalyst with 90.1% and 100% formation of CH_4 but slightly decrease for Ru/Fe/Ba (5:30:65)/Al_2O_3 catalyst which only gave 69.3% conversion of CO_2 with 66.1% formation of CH_4 at high reaction temperature of 300 °C. For this ratio, Ru/Fe/Sr (5:30:65)/Al_2O_3 catalyst gave almost 90% conversions of CO_2. Toemen *et al.* had discussed that the addition of Sr did not modify the crystalline structure of the catalyst but gave higher surface area, smaller particle size and high metal dispersion as well as increased the degree of reduction and CO chemisorption.

Table 2 Conversion of CO_2 over various alumina supported alkaline earth metal oxide-based catalysts calcined at 1000° C for 5 hours

Alumina supported catalyst	**Reaction temperature**					
	100 °C		**200 °C**		**300 °C**	
	CO_2 (%)	**CH_4 (%)**	**CO_2 (%)**	**CH_4 (%)**	**CO_2 (%)**	**CH_4 (%)**
Ru/Fe/Mg (5:10:85)/Al_2O_3	1.13	0.82	7.83	6.95	40.5	35.1
Ru/Fe/Ca (5:10:85)/Al_2O_3	2.28	1.62	11.6	10.2	64.6	51.6
Ru/Fe/Sr (5:10:85)/Al_2O_3	3.4	2.19	25.1	24.7	90.1	90.1
Ru/Fe/Ba (5:10:85)/Al_2O_3	2.42	1.97	20.1	18.8	69.3	66.1

From the results obtained in Table 1 and Table 2, Ru/Fe/Sr (5:10:85)/Al_2O_3 catalyst was found to be more active than others prepared catalysts. Therefore, this catalyst was used for optimization part in order to achieve high conversion of CO_2. The experimental parameters conducted on Ru/Fe/Sr (5:10:85)/Al_2O_3 catalysts include the following which is the effect of calcination temperatures and strontium oxide-based loadings. In general, all catalysts have low percentage of CO_2 conversion at the beginning of the process in ranging reaction temperature from 100°C to 200°C. When the reaction temperature reached 300°C, all catalysts show abruptly increased in CO_2 conversion. It can be observed that the highest CO_2 conversion was obtained from Ru/Fe/Sr (5:10:85)/Al_2O_3 catalyst calcined at 1000 °C with 90.1% conversion with 100% formation of CH_4, followed by catalyst calcined at 900 °C and 1100 °C which achieved only 82.7% with 100% formation of CH_4, and 50.3% of CO_2 conversion with 62.9% formation of CH_4 at 300 °C, respectively. The high catalytic activities of the catalysts are possibly attributed by the presence of small particles size (<300 nm) that indicates high surface area and agglomeration due to calcination temperature. This result is in good agreement with Chen *et al.* who suggested that the 1000°C calcinations temperature could activate the catalytic centers of the catalyst by controlling the size of metal particles and their interaction with Al_2O_3. Further increase the calcinations temperature to 1100°C would then decreasing the catalytic activity to 50.3% over this catalyst. It was due to the formation of large particle size, thus reducing surface area of catalyst that leads to low catalytic performance. The trend plot of the catalytic activity is as shown in Figure 1.

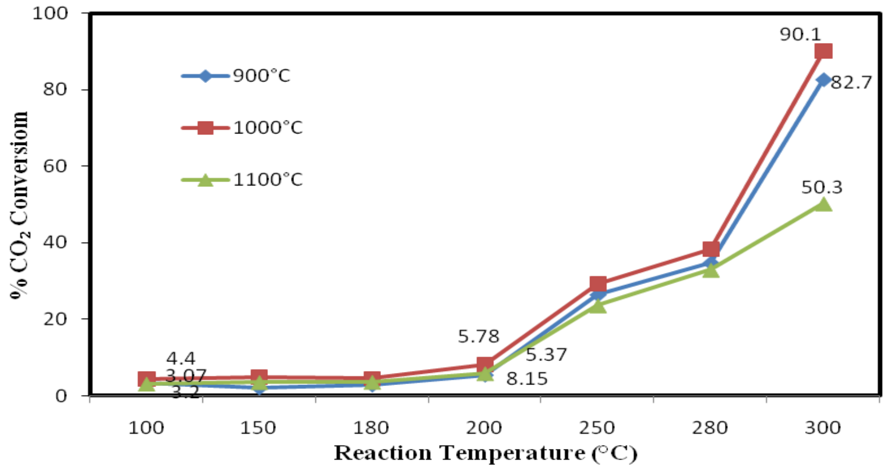


Figure 1 Catalytic performance of CO_2 conversion from methanation reaction over Ru/Fe/Sr (5:10:85)/Al_2O_3 catalyst calcined for 5 hours at different calcination temperatures.

Based on the Figure 1, it can be suggested that calcination temperature of 1000 ˚C shows the best catalytic performance. Therefore, this temperature was used for the next optimization parameter which is effect of strontium oxide-based loadings. The effect of strontium oxide loading was carried out in order to investigate the optimum loading towards the performance of CO_2 conversion. The strontium loading used was in the range of 80 - 90 wt.%. Figure 2 shows the detailed trend plot of various amounts of strontium loadings in CO_2 conversion using the Ru/Fe/Sr/Al_2O_3 catalyst. All the catalysts were calcined at 1000 ºC for 5 hours. Overall, all the prepared catalysts had lower catalytic activities at lower reaction temperature and started to increase abruptly at temperature of 250 ºC.

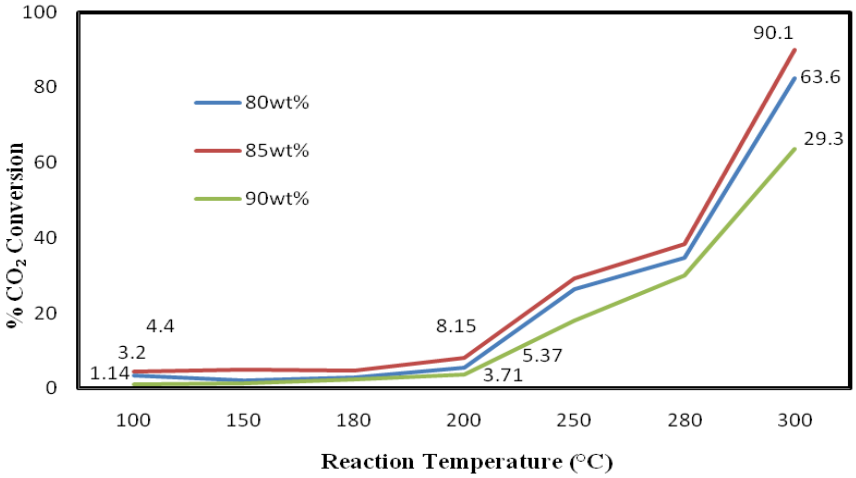


Figure 2 Catalytic performance of CO_2 conversion from methanation reaction over Ru/Fe/Sr (5:10:85)/Al_2O_3 catalyst calcined at 1000 ^{o}C for 5 hours with various loadings of strontium.

From the figure above, it was clear that the presence of strontium had significant influence on the CO_2 conversion of Ru/Fe/Sr/Al_2O_3 catalyst. Obviously, the catalytic activity increased until it reached the optimum level. At reaction temperature of 300 ^{o}C, the CO_2 conversion increased sharply from 82.3% over 80 wt.% of strontium loading to approximately 90% conversion with the strontium loading of 85 wt%. However, when the loading was increased slightly to 90 wt% (Ru/Fe/Sr (3:7:90)/Al_2O_3), the CO_2 conversion was reduced to 63.6%. Therefore, the promoting effect of CO_2 methanation was remarkably reduced with further increase in strontium loading from 80 to 90 wt.%. It was clearly showed that an appropriate amount of strontium could increase the catalytic activity of the catalyst. This is due to the addition of ceria beyond the optimal point which could result in the inhibition of CO_2 conversion. This was obviously owing to the enrichment of strontium on the catalyst surface which could cause the agglomeration to occur. . Therefore, it can be concluded that the optimum loading for strontium content was 85 wt% and followed the trend in the order of 80 wt% <85 wt% >90 wt%. Hence, Ru/Fe/Sr (5:10:85)/Al_2O_3 was chosen as the best potential catalyst.

3.2. Characterization of Potential Catalysts by Thermogravimetry Analysis (TGA)

The thermal analysis of uncalcined Ru/Fe/Mg (5:10:85)/Al_2O_3, Ru/Fe/Ca (5:10:85)/Al_2O_3, Ru/Fe/Sr (5:10:85)/Al_2O_3 and Ru/Fe/Ba (5:10:85)/Al_2O_3 catalysts has been carried out and presented in Figure 3. It can be seen that the TGA profile spectra of different alkaline earth metal-based catalyst were very similar to each other. Overall, the decomposition occurred faster at temperature between 30 ^{o}C to 450 ^{o}C and decomposed slowly until it reached the maximum temperature of 90 0^{o}C. The total weight loss over Ru/Fe/Mg (5:10:85)/Al_2O_3, Ru/Fe/Ca (5:10:85)/Al_2O_3, Ru/Fe/Sr (5:10:85)/Al_2O_3 and Ru/Fe/Ba (5:10:85)/Al_2O_3 catalysts were 22.3%, 24.3%, 23.8% and 14.7%, respectively. These sample catalysts were composed by three stages of weight loss processes in temperature ranged between 25 ^{o}C to 900 ^{o}C. The first step at temperature range of 28 ^{o}C to 130 ^{o}C represented the removal of physicall**y** adsorbed water on the surface of the catalyst. The second stage might correspond to the decomposition of hydroxyl and basic nitrate precursor was studied by Arsalanfar *et al.* [3] occurred at temperature from 130 to 450 ^{o}C. Therefore, the decomposition at this temperature may can produce water and nitrogen dioxide simultaneously. The third weight loss with onset temperature of 450^{o}C to 900^{o}C was due to the decomposition of amorphous hydroxycarbonates, $M_2CO_3(OH)_2$ which occurred at higher temperature before metal oxide was produced.

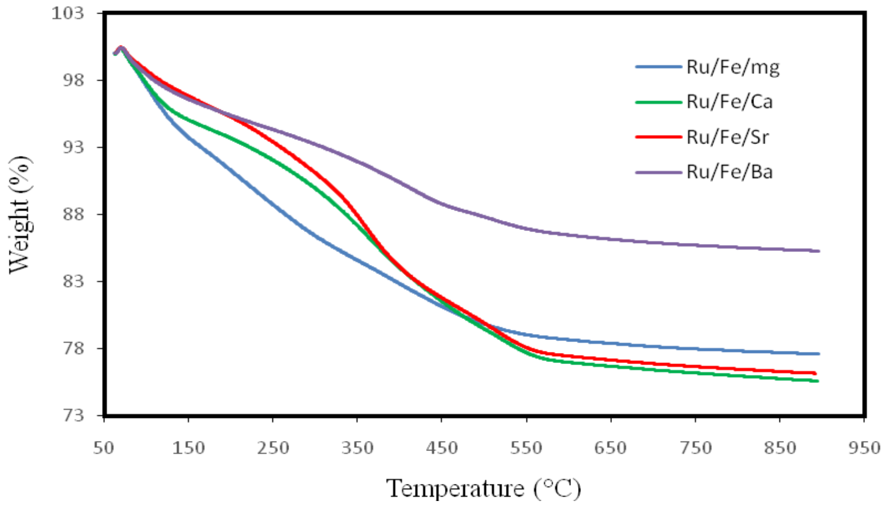


Figure 3 TGA analysis of a) Ru/Fe/Mg (5:10:85)/Al_2O_3, b) Ru/Fe/Ca (5:10:85)/Al_2O_3, c) Ru/Fe/Sr (5:10:85)/Al_2O_3 and d) Ru/Fe/Ba (5:10:85)/Al_2O_3 catalysts.

3.3. Characterization of Potential Catalysts by X-ray Diffraction (XRD)

The X-Ray Diffraction analysis was used in this research to determine the crystallinity of the catalyst, the size particle of the catalyst and the active oxide phases which contribute to the good catalytic activity.

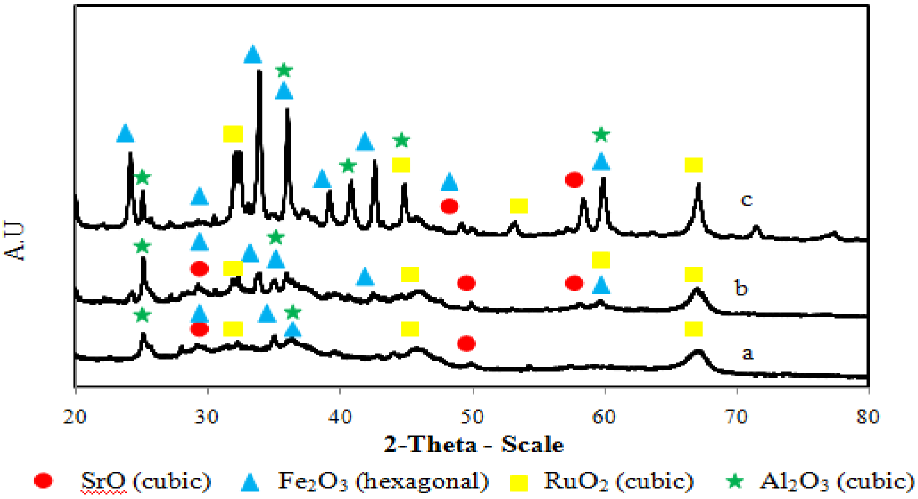
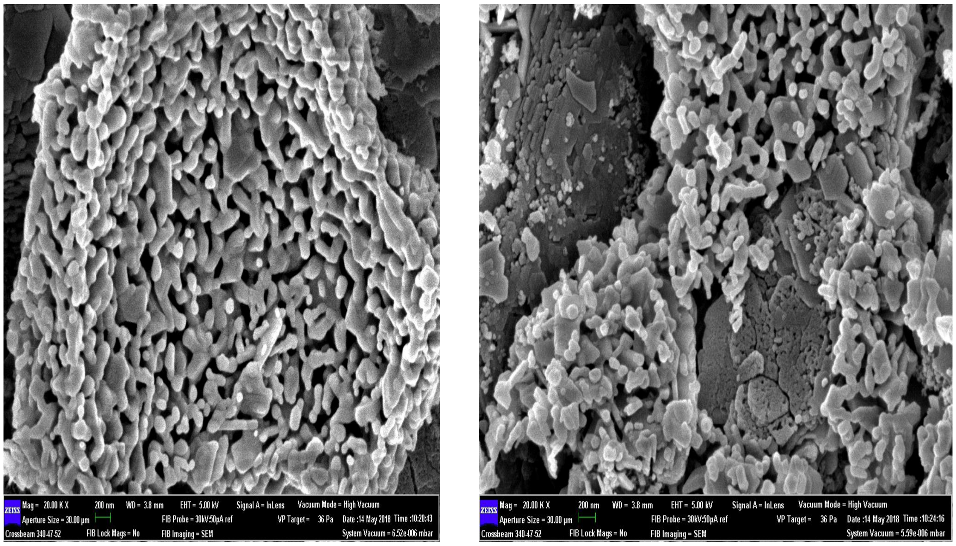


Figure 4 The diffractogram of Ru/Mn (25:75)-Al_2O_3 catalyst calcined at a) 900°C b) 1000°C and c) 1100°C.

Figure 4 shows the increase in crystallinity of fresh catalyst after series of treatment by different calcinations temperature. The peaks observed in the diffractogram are more prominent, sharper and narrower that showed the crystallinity of the catalyst increased with the increasing of calcinations temperature. Jones *et al.* claimed that catalysts calcined at temperatures above 500 ºC showed high crystallinity. It is suggesting that when the increase of calcinations temperature, there is an absent of amorphous phase and the dominant phase is the crystalline phase. The intensity was higher on samples calcined at (b) and (c) than (a) suggesting the higher crystallinity and crystallize size of sample treated at 1000 °C and 1100 °C than those treated at 900 °C. On the other hand, samples prepared at high temperature of 1100 °C and 1000 °C showed a clear pattern of metal oxide. The phase detected for the fresh catalyst was observed in catalyst calcined at 900°C was cubic Al_2O_3, cubic RuO_2, hexagonal Fe_3O_4 and cubic SrO. For fresh catalyst calcined at 1000 °C the peaks which was dominated by alumina was revealed as cubic phase at 2θ values of 25.141° (I_{20}) with d_{obs} values of 3.5392Å (d_{ref} values of 3.5300Å) conforming the presence of the alumina phase as support. For fresh catalyst calcined at 1000 °C, the characteristic peaks of the RuO_2 cubic phase at 2θ of 31.95° (I_{100}) was observed. Generally, the increase of calcinations temperature would increase the particle size; however, the increment was not prominent. The sintering process usually comes with high temperature. From the catalytic activity results, high sintering such as 1100°C calcinations temperature was sufficient to deactivate the catalytic activity of the catalyst.

3.4. Characterization of Potential Catalysts by (FESEM-EDX)

Analysis using Field Emission Scanning Electron Microscopy (FESEM) was done to observe the morphology of the catalyst surface. The best catalyst which is Ru/Fe/Sr (5:10:85)/Al_2O_3 calcined at 1000 ºC for 5 hours was chosen to further characterize using FESEM analysis. Generally, the micrographs of the supported catalysts showed a rough surface morphology. Figure 5 depicts the image of alumina supported Ru/Fe/Sr catalyst in the ratio of 5:10:85 at 1000°C in 20000 times magnification at different area.



(a) (b)

Figure 5 FESEM micrographs of alumina supported Ru/Fe/Sr catalyst in the ratio of 5:10:85 calcined at 1000°C at different area using 20000x magnifications.

From the micrograph in Figure 5 (a), it was clear that the morphology looks like staghorn coral. It was noted that the pore of the catalyst is slightly visible. It can be said that moderate pore diameter and particle size of the catalyst are important for high catalytic activity as reported by Nurunnabi *et al*. Based on Figure 5 (b), it can be observed that the particles on the spent catalyst surface are smaller and highly dispersed. This is probably because the Ru particles had been absorbed into the bulk matrix of the catalyst, thus exhibiting a well-dispersed surface and this indicates the reduction of active species on the catalyst surface. According to Safariamin *et al.* who concluded that Ru particles had been well-dispersed into the pore of the support. This result is complimented by the EDX analysis of the spent Ru/Fe/Sr (5:10:85)/Al_2O_3 calcined at 1000ºC. The element composition that contains in the alkaline earth oxide catalyst can be determined by using EDX analysis. The EDX was done on the surface of coated alumina supported to see how much of the catalyst that has successfully coated the support.

Table 3 Composition of fresh Ru/ Fe/ Sr (5:10:85)/Al_2O_3 catalyst at different calcination temperatures

Catalyst	**Calcination temperature (°C)**	**Loading (wt%)**				
		Al	**O**	**Sr**	**Fe**	**Ru**
Ru/Fe/Sr (5:10:85)/Al_2O_3	900	45.28	53.75	8.27	3.58	1.74
Ru/Fe/Sr (5:10:85)/Al_2O_3	1000	42.08	46.46	9.32	5.6	2.57
Ru/Fe/Sr (5:10:85)/Al_2O_3	1100	47.5	50.26	7.48	6.56	0.37

4. CONCLUSION

Results obtained from the catalytic activity measurement using an in-house-built reactor show that Ru/Fe/Sr (5:10:85)/Al_2O_3 calcined at 1000°C gave a high CO_2 conversion and is able to give high percentage yield of CH_4 at low reaction temperature of 300 °C which are 90.1% and 100%, respectively. Therefore, it was indicated that this catalyst is a promising catalyst for carbon dioxide methanation reaction. An XRD analysis showed that the catalyst showed a polycrystalline structure with the mixture of SrO, Fe_2O_3, RuO_2 and Al_2O_3. It was also proposed that RuO_2 and SrO in cubic, and Fe_2O_3 in hexagonal are the active species of the Ru/Fe/Sr (5:10:85)-Al_2O_3 catalyst. Besides that, it was also noted that the Al_2O_3 phase should be cubic for the catalyst to achieve high catalytic activity towards CO_2 methanation reaction. The FESEM micrograph showed the surface of the Ru/Fe/Sr (5:10:85)/Al_2O_3 catalyst calcined at 1000 °C looks like a staghorn coral shape. It is believed that a small particle size lays an important role to achieve higher catalytic activity. From the EDX analysis, the surface area of the used Ru/Fe/Sr (5:10:85)/Al_2O_3 catalyst showed a reduction of 2.57% of Ru, 5.6% of Fe and 9.32% of Sr content, respectively. In conclusion, the objectives of this work were successfully achieved, whereby high CO_2 conversion and high yield of methane were achieved at low reaction temperature (300ºC).

REFERENCES

[1] Clem E. Powell and Greg G. Qiao (2013). Polymeric CO_2/N_2 Gas Separation Membranes for the Capture of Carbon Dioxide from Power Plant Flue Gases. *Journal of Membrane Science.* 279, 1–49.

[2] Maimoon. Atif, Fahad A. Al-Sulaiman (2017). Energy Analyses of Solar Tower Power Plant Driven Supercritical Carbon Dioxide Recompression Cycles for Six Different Locations. *Renewable and Sustainable Energy Reviews.* 68, 153-167.

[3] Arsalanfar, M., Mirzaei and Pourdolant (2012). Structural Characteristics of Supported Cobalt-Cerium Oxide Catalysts Used in Fischer-Tropsch Synthesis. *Journal of Natural Gas Science and Engineering.* 9, 119-118.

[4] Jones, C., Cole, K.J., Taylor, S.H., Crudace, M.J. and Hutchings, G.J. (2009). Copper manganese oxide catalysts for ambient temperature carbon monoxide oxidation: Effect of calcination on activity. *Journal of Molecular Catalysis A: Chemical*. 305, 121-124.

[5] Nurunnabi, M., Murata, K., Okabe, K., Inaba, M. and Takahara, I. (2008). Performance and characterization of Ru/Al_2O_3 and Ru/SiO_2 catalysts modified with Mn for Fischer–Tropsch synthesis. *Applied Catalysis A: General*. 340, 203-211.

[6] Safariamin, M., Tidahy, L.H., Abi-Aad, E., Siffert, S. and Aboukais, A, (2009), Dry reforming of methane in the presence of ruthenium-based catalysts, *Comp. Rend. Chim.* 12, 748-753.