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# Methanation Reaction over Samarium Oxide Based Catalysts

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## ABSTRACT

Malaysia produces an acidic crude natural gas which contains 23% of $CO_2$ and <1% of $H_2S$. Thu their presence will corrode the carbon steel gas pipeline system, thus resulting decreasing quality and price of natural gas as well as pollute the environment. Instead, using catalysts for the $CO_2$ methanation have been extensively studied and high potentiality towards converting $CO_2$ gas to methane. The potential of samarium has been widely explored for their ability as a dopant catalyst for $CO_2$ methanation from researchers for metal oxide in $CO_2$ methanation. However, the potential of samarium as a based catalyst in $CO_2$ methanation have not been explored yet. Therefore, in this study the supported samarium oxide doped transition metals catalysts was prepared by wetness impregnation method for carbon dioxide methanation reaction by using trimetallic oxide catalyst because of the lower performance of conversion of $CO_2$ in monometallic oxide and bimetallic oxide catalysts. The catalytic activity of prepared catalysts was tested using in-house built micro reactor coupled with Fourier Transform Infrared (FTIR) toward $CO_2/H_2$ methanation. Then, the catalysts were optimized by different calcination temperatures and different based oxide loadings. The potential catalysts of Ru/Mn/Sm (5:35:60)/$Al_2O_3$ calcined at 1000 °C and 1100 °C gave > 95 % of $CO_2$ conversion at 300 °C reaction temperature and yielded about 93.46 % of $CH_4$ at reaction temperature of 400 °C. XRD analysis showed the potential catalysts are an amorphous phase, while FESEM analysis illustrated the surface of the catalysts were covered with small and dispersed spherical particles. EDX analysis revealed that there were 0.3 % reduction of Ru in the Ru/Mn/Sm (5:35:60)/$Al_2O_3$ ofused catalysts compared to fresh catalysts. Meanwhile NA analysis showed that Ru/Mn/Sm (5:35:60)/$Al_2O_3$ catalystattained surface area of 47.38 $m^2$/g.

| carbon dioxide | methanation | catalyst | trimetallic oxide |

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## 1. INTRODUCTION

Natural gas nowadays, is amongst one of the fastest growing component of the world primary energy consumption. About 70 % of the electricity generated in Malaysia by year 2000 comes from the natural gas [1]. The principle constituent of natural gas is methane. However, it also contains other hydrocarbons such as ethane, and propane and also non-hydrocarbon components such as carbon dioxide, hydrogen sulfide and helium [2]. The acid gas of carbon dioxide in natural gas will not only declined the quality of the natural gas but also can be harmful to the environment. Therefore, natural gas needed to be purified in order to eliminate the acid gases before it can be used.

Therefore, the focus has now shifted to the more promising method which is the catalytic conversion systems. The essential requirement for the correct selection of the oxide system is its ability to accept and to activate $CO_2$. The acid nature of $CO_2$ necessitates the employment of a catalytic system with the basic properties [3]. Samarium had not yet been widely explored for their ability as a base catalyst for $CO_2$ methanation but they had received attention from researchers as dopant material for metal oxide in $CO_2$methanation [4]. From previous research done by Yamasaki *et al*. (1999), they have been reported that amorphous alloys of Ni–25Zr–5Sm reached 90 % conversion of $CO_2$ and the $CH_4$ selectivity was 100 % at 300 °C [5].

Samarium oxide alsohas a potential as a dopant in carbon methanation as reported by Zhou Chunhui *et al*. The addition of Sm to Ba-Ru-K/AC (active carbon) improved significantly the activity and stability of the catalyst. This indicated that samarium impeded the adsorption of hydrogen on the catalyst surface, thus leading to the high catalytic activity and resistance to carbon methanation. Furthermore, XRD results revealed that the promoter samarium was in the form of both samarium oxide and carbonide ($Sm_2C1–x$). The formation of $Sm_2C1–x$ was probably due to the interaction of samarium with the unsaturated bond of carbon, and thus hindered the carbon-methanation [6].

Another research has been done on $CO_2$ methanation catalysts prepared from amourphous Ni-Zr-Sm by Michiaki Y. et al. This catalyst showed higher catalytic activity for methanation of carbon dioxide than a conventional prepared zirconia supported nickel catalyst.The stabilization of tetragonal zirconia and the increase number of active surface nickel sites by addition samarium lead to enhancement of catalytic activity. As for zirconia, samarium oxide is regardedas good supports of nickel catalyst for methanation of carbon dioxide [7].

Therefore, in this study samarium was chosen due to their unique properties and also because of the basic properties of the lanthanide.

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## 2. EXPERIMENTAL

### 2.1 Preparation of Catalysts *via* Wetness Impregnation Method

In this research, the catalysts were prepared employing the wetness impregnation technique usingManganese nitrate tetrahydrate, $Mn(NO_3)_2•6H_2O$ and cobalt nitrate 6-Hydrate,$Co(NO_3)_2•6H_2O$as the dopant and ruthenium (III) chloride hydrate, $RuCl_{3.}H_2O$ as co-dopant. Each of metal salts was weighed according to desired ratio. The base metal precursor was prepared by dissolving samarium (III) nitrate hexahydrate, $Sm(NO_3)_{3.}6H_2O$ (5.00 g) with distilled water in a small by droplet as minimum as can. Then thedopant and co-dopant salt were then dissolved with distiled water and stirred with magnetic stirrer about 20 minutes. Finally, alumina was impregnated into the solution for 30 minutes. The supported catalyst were transferred on glass wool in evaporating dish, aged inside the oven at 80-90 °C for 24 hours and later calcined for 5 hours at 400 ºC. The same preparation process has been repeated in optimizing the based oxide loading and calcination temperature.

### 2.2 Catalytic Performance Test

All prepared catalysts were tested for their catalytic activity towards carbon dioxide methanation reaction by using in-house-built micro reactor. The analysis was conducted using simulated natural gas comprising of continuous flow of $CO_2$ and $H_2$ (1:4) mixture with composition 20% $CO_2$ and 80% $H_2$, and flow rate of 50 mL/min. This reactor was coupled with Fourier Transform Infra Red (FTIR) Nicolet Avatar 370 DTGS. The formation of methane was detected by Hewlett-Packard 6890 Series GC System (Ultra 1) with 25.0 m × 200 µm × 0.11 µm nominal columns, helium gas as the carrier gas with flow rate of 20 mL/min at 75 kPa, and using Flame Ionization Detector (FID). The measurements were done at reaction temperatures of 100ºC, 200ºC, 300ºC and 400ºC.

### 2.3 Characterization of the Metal Supported Catalysts

The characterizations were studied by X-ray Diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM), Energy Dispersive X-Ray (EDX), and Nitrogen Adsorption/desorption (NA). XRD analysis was done by using Diffractometer D5000 Siemens Crystalloflex with CuKα radiation (λ=1.54060A). Scans were performed in step mode of 0.20 seconds/step. For FESEM analysis, sample was scanned using Zeiss Supra 35 VP FESEM operating of 15 kV, couple with EDX analyzer and 1500× magnification. The catalyst sample was bombarded by electron gun with tungsten filament under 25 kV. N2 adsorption-desorption isotherms for the catalysts were measured by Micromeritics ASAP 2010 after degassing at 120°C. Nitrogen gas with the flow rate 50 µL/min was used as the atmosphere.

## 3. RESULTS & DISCUSSION

### 3.1. Catalytic Performance of Alumina Supported Samarium Oxide Catalyst Calcined at 400°C

The trends of $CO_2$ conversion for the alumina supported samarium oxide based catalyst with Mn and Co dopants are shown in Fig. 1.The series of samarium oxide catalyst was screening at 400 °C calcination temperature for catalytic activity performance. Both mono and bimetallic oxide catalysts showed low performance of catalytic activity. The study was then conducted by using additional dopant (manganese and cobalt) in order to observe the effect of dopant towards the catalytic activity of alumina supported samarium oxide catalysts.According to Xavier K. O. *et al.*, incorporation of dopant is expected to increase the catalytic performance of the catalyst by enhancing the intrinsic activity [8].

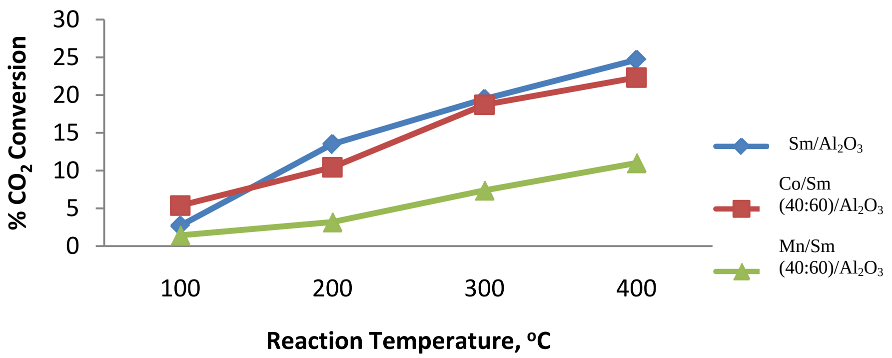

**Fig. 1.** Catalytic performance of $Sm/Al_2O_3$, $Mn/Sm$ (40:60)/$Al_2O_3$, and $Co/Sm$ (40:60)/$Al_2O_3$, catalysts calcined at 400°C for $CO_2$ /$H_2$ methanation reaction.

Meanwhile, for trimetallic oxide catalyst, Ru/Mn/Sm (5:35:60)/ $Al_2O_3$ showed the highest of $CO_2$ conversion which is 96.29 %. Table 1 summarizes the $CO_2$ conversion forRu/Mn/Sm (5:35:60)/$Al_2O_3$, and Ru/Co/Sm (5:35:60)/$Al_2O_3$ catalysts. All of the corresponding catalysts showed an increasing percentage of $CO_2$ conversion with respect to the increased in reaction temperature. Nevertheless, Ru/Mn/Sm (5:35:60)/$Al_2O_3$ catalyst display tremendous increasing $CO_2$ conversion starting at reaction temperature of 200 °C to 400°C while Ru/Co/Sm (5:35:60)/$Al_2O_3$ increased gradually starting from 300 °C of reaction temperature.All prepared catalysts showed an increasing percentage of $CO_2$ conversion with respect to increase reaction temperature. The catalysts doped with Ru/Mn showed higher percentage of conversion than Ru/Co because Mn species could remove Cl atom from $RuCl_3$precursor hence increased the density of active Ru oxide species [9]. Therefore,the potential catalysts of Ru/Mn/Sm (5:35:60)/$Al_2O_3$ was optimized and screened for their catalytic activity.

The methanation reaction using Ru/Mn/Sm (5:35:60)/$Al_2O_3$ catalyst showed the highest percentage of $CO_2$ conversion with 96.29 % followed by Ru/Co/Sm (5:35:60)/$Al_2O_3$ catalysts with 55.98 %. The addition of Ru as co-dopant increased the percentage of $CO_2$ conversion of catalytic activity. This might due to the small atomic size of Ru (134 pm) that dispersed well on metal oxide carriers and exhibit higher activity for methanation [10].

### 3.2.1 Catalytic Performance Optimization of Alumina Supported Samarium Oxide Based CatalystsCalcined at Various Temperatures

Then the catalysts were prepared with different calcination temperatures; 400 °C, 700 °C and 1000°C in order to observe the effects of calcination temperature towards the catalytic performance. Table2 showspercentage of $CO_2$ conversion for Ru/Mn/Sm (5:35:60)/$Al_2O_3$ catalyst at various temperature. The percentage of $CO_2$ conversion started to increase at reaction temperature of 200 °C. Ru/Mn/Sm (5:35:60)/$Al_2O_3$ catalyst achieved 100 % of $CO_2$ conversion when calcined at 1000 °C. Table 2 also show the percentage of $CO_2$ conversion for Ru/Co/Sm (5:35:60)/ $Al_2O_3$ catalyst at various temperatures.

Table 2 summarizes the catalytic activity of $CO_2$ conversion temperatures.The percentage conversion of $CO_2$ increased when the calcination temperature increased. Ru/Mn/Sm (5:35:60)/$Al_2O_3$ catalyst achieved 100 % conversion of $CO_2$ when calcined at 1000 °C whereas Ru/Mn/Sm (5:35:60)/$Al_2O_3$ catalyst achieved 100 % conversion of $CO_2$ when calcined at 700 °C and 1000 °C. This result suggested that the high calcination temperature activates the catalytic centres of the catalyst, thus enhancing the activity. The calcination temperatures are critical for controlling the size of the metal particles and their interaction with $Al_2O_3$ as suggested by Chen *et al.* who investigated the effect of calcination temperatures on methane decomposition. It was found that when the calcination temperature is increased, the average size of the crystalliteincreases ascendingly [11].

### 3.2.2 Catalytic PerformanceOptimization of Alumina Supported Samarium Oxide Based Catalyst by Based Loading

Fig. 2 shows the catalytic performance of alumina supported Ru/Mn/Sm catalyst calcined at 1000 °C. Ru/Mn/Sm (5:35:60)/$Al_2O_3$, Ru/Mn/Sm (5:30:65)/$Al_2O_3$ and Ru/Mn/Sm (5:25:70)/$Al_2O_3$ showed 100 % of $CO_2$ conversion while the percentage conversion $CO_2$ for Ru/Mn/Sm (5:20:75)/$Al_2O_3$, Ru/Mn/Sm (5:15:80)/$Al_2O_3$ and Ru/Mn/Sm (5:10:85)/$Al_2O_3$ were reduced to 98.99 %, 98.18 % and 95.56 % respectively. The catalytic performances of the catalysts were reduced as the amount of based oxide loading increased. It was possibly due to the blockage of active sites which were hindered by the introduction of excess amount of the metal oxide.

The reduction of catalytic activity performance as the amount of based oxide loading increased is in agreement with previous research done by Zhao A. *et al.* which the conversion of CO increased rapidly from 43.6 % to 74.80 % with the increase of lanthanide from 0-2 wt % but further addition of lanthanide resulted in a drastic decrease of CO. The loss of activity with higher lanthanide content is due to the blockage of active sites by excess amount of lanthanide introduced to the catalyst [12]. It is also due to the decreasing of the manganese ratio in the catalysts as manganese is a good reducing agent which enhances the reduction of $CO_2$ to methane.

**Table 1**. Percentage conversion of $CO_2$ catalysed by Ru/Mn/Sm (5:35:60)/$Al_2O_3$, and Ru/Co/Sm (5:35:60)/$Al_2O_3$ catalysts.

| **Catalysts** | **Reaction Temperature** | | | |
|---|---|---|---|---|
| | **100°C** | **200°C** | **300°C** | **400°C** |
| | **% $CO_2$Conversion** | | | |
| Ru/Mn/Sm (5:35:60)/$Al_2O_3$ | 0.32 | 2.05 | 48.88 | 96.29 |
| Ru/Co/Sm (5:35:60)/$Al_2O_3$ | 1.68 | 1.86 | 10.09 | 55.98 |

**Table 2**. Percentage conversion of $CO_2/H_2$ catalysed by Ru/Mn/Sm (5:35:60)/$Al_2O_3$ catalyst calcined at 400 °C, 700 °C and 1000 °C for 5 hour.

| Catalyst | Calcination Temperature (ºC) | Reaction Temperature (ºC) | | | |
|---|---|---|---|---|---|
| | | 100ºC | 200ºC | 300ºC | 400ºC |
| | | % $CO_2$ Conversion | | | |
| Ru/Mn/Sm (5:35:60)/$Al_2O_3$ | 400 | 0.32 | 2.05 | 48.88 | 96.29 |
| | 700 | 3.38 | 4.37 | 61.04 | 96.69 |
| | 900 | 0.91 | 1.35 | 70.28 | 91.57 |
| | 1000 | 0.31 | 3.68 | 95.53 | 100.00 |
| | 1100 | 13.39 | 80.53 | 96.77 | 99.35 |
| Ru/Co/Sm (5:35:60)/$Al_2O_3$ | 400 | 1.68 | 1.86 | 10.09 | 55.98 |
| | 700 | 0.97 | 27.80 | 42.29 | 65.58 |
| | 900 | 3.85 | 13.09 | 22.60 | 74.53 |
| | 1000 | 8.33 | 17.70 | 44.46 | 85.45 |
| | 1100 | 0.29 | 18.69 | 34.92 | 89.73 |

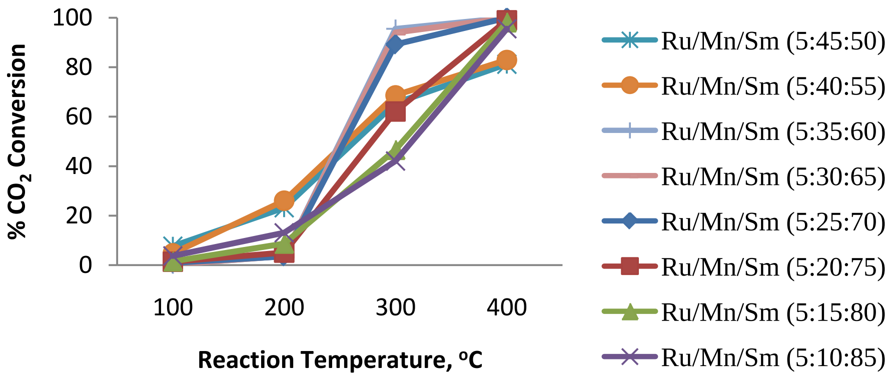

**Fig. 2**. Catalytic performance of alumina supported Ru/Mn/Sm catalyst calcined at 1000 °C with various loading of samarium oxide.

### 3.3 Detection of Methane by Gas Chromatography for $CO_2$ Methanation Reaction

The potential catalyst selected from the preliminary testing was further studied for their $CO_2/H_2$ methanation activity. The Ru/Mn/Sm (5:35:60)/$Al_2O_3$catalyst calcined at 1000ºC was considered as the potential catalyst for $CO_2$ methanation reaction since it gave 100 % of $CO_2$ conversion with 93.46 % of $CH_4$ yield at reaction temperature of 400ºC. Fig. 3 shows that at initial temperature of 100°C and 200 °C nomethane products were produced. However, at reaction temperature of 300 °C,Ru/Mn/Sm (5:35:60)/$Al_2O_3$catalyst yielded about78.22 %. High formation of methane at high reaction temperature is due to its highly exothermic reaction where the methanation reaction is favourably occurred at high temperature.

### 3.4 Characterization of the Ru/Mn/Sm (5:35:60)/$Al_2O_3$ Supported Catalyst

XRD analysis in Fig. 4 shows the potential Ru/Mn/Sm (5:35:60)/$Al_2O_3$ catalyst calcined at various temperatures. From the figure, it is observed that the degree of crystallinity of the catalyst is improved as the calcination temperature increased (400 ºC, 700 ºC, 1000 ºC).From the XRD diffractogram, at 1000ºC calcination temperature the peaks having moderate degree of crystallinity and these contribute to the high catalytic activity which 100% $CO_2$ conversion. This result is in agreement with Lercher J.A. *et al* which stated that the maximum percentage of $CO_2$ conversion achieved as the average size of the crystallite increased when the calcination temperature increased [13].

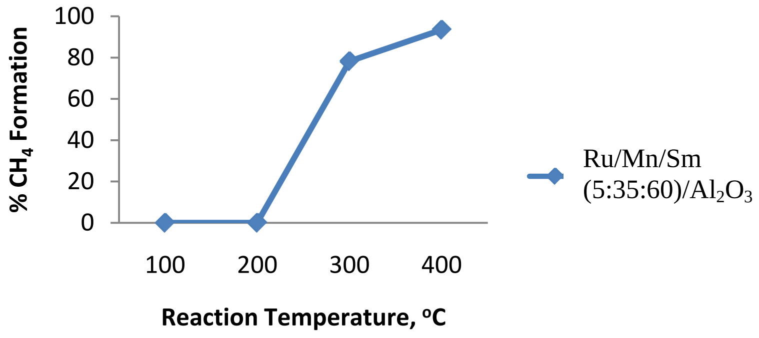

**Fig. 3.** The plots of $CH_4$ formation over Ru/Mn/Sm (5:35:60)/$Al_2O_3$ catalyst calcined at 1000 °C for 5 hours.

This indicates that the catalyst has small particle size and large surface area that contribute to the high catalytic activity at 1000°C of calcinationtemperature.Thereveal peaks at 400°C are due to the presence of $Al_2O_3$ of cubic phase which reveal at 2θ values of 66.862° ($I_{100}$) and 37.379° ($I_{40}$) (2$\theta_{ref}$ values: 67.307° and 37.442°) with $d^*_{obs}$ values (Å) of 1.398° and 2.396° ($d^*_{ref}$ values (Å): 1.399 and 2.394). On behalf of Ru/Mn/Sm (5/35/60)/$Al_2O_3$ catalyst calcined at 700 °C, the peak of alumina cubic phase can be assigned at 2θ values of 66.746° ($I_{100}$), and 37.354° ($I_{40}$) (2$\theta_{ref}$ values: 67.307° and 37.442°) with $d^*_{obs}$ values (Å) of 1.400, and 2.387 ($d^*_{ref}$ values (Å): 1.399 and 2.394).

Meanwhile, Ru/Mn/Sm (5/35/60)/$Al_2O_3$ catalyst calcined at 1000 °C shows alumina cubic peaks at 2θ values of 66.852° ($I_{100}$), 37.212° ($I_{40}$), 45.799° ($I_{20}$) and 60.546° ($I_{10}$) (2$\theta_{ref}$ values: 67.307°, 37.442°, 45.790° and 60.459°) with $d^*_{obs}$ values (Å) of 1.398, 2.414, 1.980 and 1.527 ($d^*_{ref}$ values (Å): 1.399, 2.394, 1.979 and 1.528).The peak of diffractogram is supported by FESEM that is nanoparticle and not highly homogenous.

FESEM analysis in Fig. 5 shows the surfaces of catalyst was covered with small and dispersed spherical particles. The catalysts were densely agglomerated. The particle size for Ru/Mn/Sm (5:35:60)/$Al_2O_3$ catalyst is in range from 160.8 nm to 263.5 nm. Moderate pore diameter and small particle size of the catalyst are important for high catalytic activity [14]. This is agreedwiththeXRD analysiswhichexhibitedvery broad peaks denoting an amorphous character for the Ru/Mn/Sm (5:35:60)/$Al_2O_3$ catalyst calcined at 1000°C.

From the Fig.5, the fresh Ru/Mn/Sm (5:35:60)/$Al_2O_3$ catalyst shows rough surface morphology with inhomogeneous spherical shape and comes with small particles sizes. The morphology of fresh catalyst changed significantly after the hydrogenation of methanation reaction which showed the formation of aggregated and agglomerated undefined shape on the surface of spent catalyst. This observation is possibly due to the heat generated during the catalytic reaction which caused the catalyst to form agglomerated thus decreasing the activity [15].The formation of aggregated and agglomerated making the used catalyst increased its particle size and having larger interaction between metal and support catalyst.

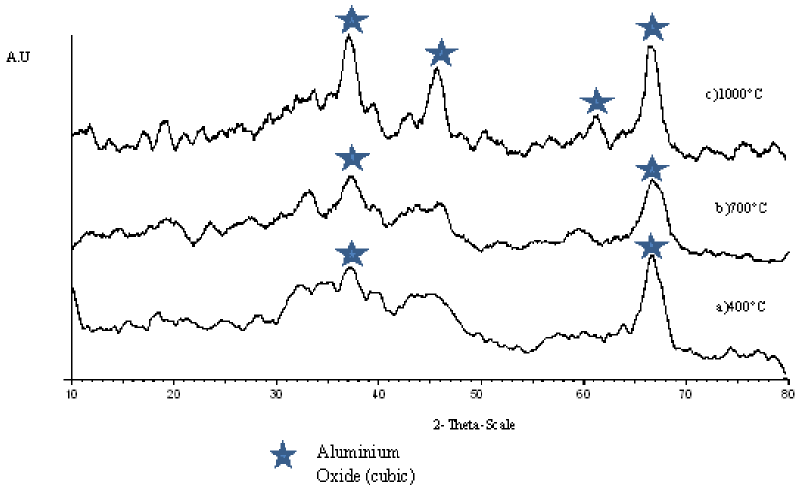

**Fig. 4.** XRD Diffractogram of Ru/Mn/Sm (5/35/60)/$Al_2O_3$ catalyst calcined at various temperatures; 400 °C, 700 °C and 1000 °C for 5 hours.

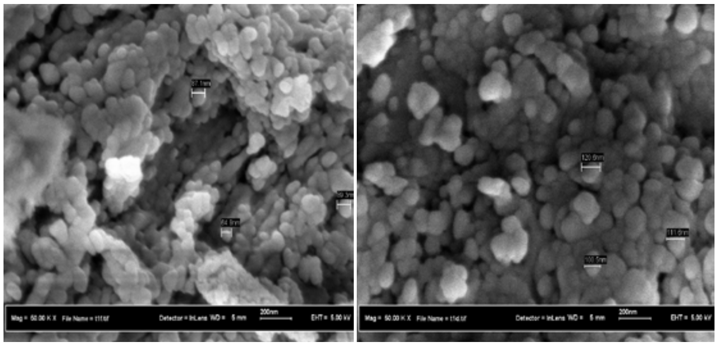

**Fig. 5.** FESEM micrograph of Ru/Mn/Sm (5/35/60)/$Al_2O_3$ catalysts: a) fresh, and b) used catalysts calcined at 1000ºC in 50000x magnification, scale bar; 200 nm.

**Table 3.** EDX analysis of Ru/Mn/Sm (5/35/60)/$Al_2O_3$catalyst calcined at 1000 $^{o}$C for 5 hours.

| Catalyst | Mass ratio (%) | | | | |
|---|---|---|---|---|---|
| | **Al** | **O** | **Ru** | **Mn** | **Sm** |
| Ru/Mn/Sm (5/35/60)/$Al_2O_3$(fresh) | 34.56 | 53.11 | 0.37 | 0.79 | 0.72 |
| Ru/Mn/Sm (5/35/60)/$Al_2O_3$(used) | 31.52 | 49.07 | 0.07 | 0.99 | 0.66 |

EDX analysis in Table 3 reveals that there was 0.3 % reduction of Ru in the Ru/Mn/Sm (5:35:60)/$Al_2O_3$ used catalysts compared to fresh catalysts. The reduction was due to migration of Ru into porous support during the reaction. The weight percentage of Ru on the catalyst surface may also be attributable to the high catalytic activity towards the methanation reaction, which is highly favored in the presence of Ru [16]. As seen in the Table 3, the Al peak is the highest peak which suggested that the catalyst surface is dominated by the Al from the support and the catalyst is not well dispersed on the alumina support as shown in FESEM analysis. This may be due to the noble metal and Mn being absorbed into the high porosity and high surface area alumina beads [17, 18, and 19].

The results from the EDX analysis of Ru/Mn/Sm (60:35:5)/$Al_2O_3$ catalyst suggested that the weight percentage of Mn in the fresh catalyst is the highest compared to Sm and Mn as summarizes in Table 3. Although Sm is the base catalyst and has higher ratio, Mn was found to be of higher percentage on the catalyst surface due to high affinity of Mn to be absorbed into the pores of the alumina, thus resulting in higher Mn percentage on the surface. From the Table 3 also, there was a drastic change in the weight percentage of Ru for the used Ru/Mn/Sm (60:35:5)/$Al_2O_3$ catalyst. This may be due to the migration of Ru into the bulk matrix of the catalyst surface. This result is in agreement with the finding observed by Nurunnabi *et al.* who claimed that Ru may have been absorbed into the porous support hence lower concentration of Ru on the surface [17].

In addition, NA analysis in Table 4 shows that Ru/Mn/Sm (5:35:60)/$Al_2O_3$ catalystattained surface area of 47.38 $m^2$/g. The surface area decreased as the calcination temperature increased due to the agglomeration of metallic oxide at high temperature. According to the Wan Abu Bakar *et al.* (2009), the BET surface area is presumed to be reduced when there is no generation of new active sites and no transformation of active species occurred during the catalytic reaction [19]. The calcination temperatures are critical for controlling the size of the metal particles and their interaction with $Al_2O_3$ as suggested by Chen *et al.* (2009) who investigated the effect of calcination temperatures on methane decomposition [20].Although higher calcination temperature reduced the BET surface area, yet it has the benefit of securing the existence of stable structure on the catalyst and also a promising in the better catalytic performance of the catalyst.

## 4. CONCLUSION

Ru/Mn/Sm (5:35:60)/$Al_2O_3$ catalyst calcined at 1000 °C prepared by impregnation method were chosen as the best catalysts for $CO_2/H_2$ methanation. Ru/Mn/Sm (5:35:60)/$Al_2O_3$ catalyst gives 100 % of $CO_2$ conversion with 93.46 % $CH_4$ yield. FESEM micrograph of Ru/Mn/Sm (5:35:60)/$Al_2O_3$ catalyst showed that the catalystis in small size and not homogeneous. The small particle size is confirmed by the XRD analysis which showed broad peaks of alumina cubic phase which indicate the catalysts is an amorphous phase.

**Table 4.** BET surface area and average pore diameter of the Ru/Mn/Sm (5:35:60)/$Al_2O_3$ catalyst calcined at 400 °C, 700 °C, and 1000 °C for 5 hours

| Catalyst | Calcination temperature (°C) | Surface area ($m^2$/g) |
|---|---|---|
| Ru/Mn/Sm (5:35:60)/$Al_2O_3$ | 400 | 232.55 |
| | 700 | 168.33 |
| | 1000 | 47.38 |

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