Investigation of Carbon Dioxide Methanation over Ceria Based Catalysts

Wan Azelee Wan Abu Bakar*, Susilawati Toemen, Rusmidah Ali

Department of Chemistry, Faculty of Science, UTM, 81310 UTM Johor Bahru, Johor, Malaysia

*Corresponding author: wanazelee@kimia.fs.utm.my

1.0 INTRODUCTION

According to United Nations Development Report (2007), Malaysia ranked as the 26th largest greenhouse gases emitters with the population over 27 million people. The major contributor of greenhouse gases is from power plant station since, the chemical composition of Connaught Bridge Burning Power Plant (Selangor, Malaysia) flue gases contained mainly of carbon
dioxide and water vapour. This showed that removing CO2 gases from that type of plant is very important for maintaining a green environment. Therefore, the recycling technology by the catalytic conversion is one of the most promising techniques for the CO2 treatment of gas burning power plant flue gases since the production of CH4 can also be used as a fuel to run turbine for electricity. By recycling the CO2 via this technique, the amount of natural gas needed for the combustion in a gas turbine can be reduced as well as CO2 emissions. In order for this method to be effective, the production of catalysts and its behaviour should be investigated further.

The current technologies that has been investigated by many researchers for the treatment of carbon dioxide in power plant flue gases is Integrated Gasification Combined Cycle (IGCC) which involved high maintenance fees which is not cost effective.1 In fact, there is no method applied to remove CO2 in gas power plant flue gases and also there is no research done that used catalyst under this condition. Thus, a new technology that is the catalytic conversion method made from ceria, CeO2 catalyst is introduced in this research.

Many researchers prefer to use Ni-based alumina supported system which is the traditional catalyst used for methanation.2-4 One of the reasons is because Ni is cheap and is proven to be able in producing high CO2 conversion only at higher reaction temperature. However, the drawback of Ni catalyst is to produce high CO2 conversion at possible low reaction temperature and its reproducibility properties. This is agreed by Wan Azelee et al.5 in his research using Pd/Ru/Ni (2:8:90)/Al2O3 catalyst calcined at 400°C. After underwent 4th test of reproducibility testing, Pd/Ru/Ni (2:8:90)/Al2O3 catalyst calcined at 400°C gave only 26.17% CO2 conversion compared to the fresh catalyst which was 43.60% at reaction temperature 200°C. Therefore, a new catalyst that have potential to convert CO2 to CH4 at lower reaction temperature need to be found and therefore manganese was chosen as an alternative methanation catalyst.

Research done by Seok et al.6 had proved that the presence of manganese improves the stability and durability of catalysts in CO2 reforming of methane. The addition of Mn to Ni/Al2O3 promoted the adsorption of CO2 by forming the carbonate species and it was responsible for suppression of carbon deposition over Ni/MnO-Ni/Al2O3 catalyst. Other research done by Li et al.7 showed that when manganese was doped in appropriate amount, it caused disorder in the spinal structure of metal surface and enhanced the catalytic activity of the reactive species.

Besides, the Ru/Mn is an active catalyst for methanation process but not cost effective material because of the expensiveness of Ru and therefore hardly applied for practical. To overcome this problem, we have used the ceria as based catalyst so that the usage of Ru can be reduced and the methanation activity can be improved.

Currently, ceria is known as sulphur resistant catalyst and widely being used as carrier due to its unique acid–base and redox properties.8 It is well known that ceria can affect the thermal and structural stability of the catalyst support, the dispersion of supported metal and the decrease of carbon formation on the catalyst surface.9,10 In addition, a highly basic catalyst such as CeO2 is proposed to enhance carbon dioxide adsorption and chemisorptions on the catalyst surface. It has excellent redox properties owing to the very fast reduction of Ce4+/Ce3+, which is associated with the formation of oxygen vacancies at the surface.11 However, the pure ceria hardly produced high activity of CO2 methanation, therefore, the addition of ceria to Ru/Mn/Al2O3 catalyst was prepared. The structure, physicochemical properties and catalytic activity of the catalyst was investigated intensively.

2.0 EXPERIMENTAL

2.1 Preparation of Catalysts

All the catalysts were prepared by aqueous incipient wetness impregnation method. 5 g of Ce(NO3)3·2H2O obtained from MERCK was dissolved in small amount of distilled water. Mixed catalyst solution was prepared by mixing an appropriate amount of second or third metals such as Ru and Mn nitrate salts (Sigma Aldrich) with Ce(NO3)3·2H2O solution according to its ratio. A homogeneous mixture was obtained by electromagnetic stirring at room temperature for 30 minutes. Alumina beads with diameter of 3 mm were used as support material in this study. The support was immersed into the catalysts solution until the solution was evenly absorbed on the surface of the support. The coating process was repeated three times with drying at ambient temperature for every coating process. It was then aged inside an oven at 80–90°C for 24 hours followed by calcinations using a furnace in the air atmosphere at 1000°C for 5 hours using a ramp rate of 10°C/min to remove all the metal counter ions and water present in the catalyst. Lastly, the sample was labelled as Ru/Mn/Ce-65/Al2O3 denoting there is 65 wt% of Ce, 30wt% of Mn and 5 wt% of Ru. Similar procedure was repeated for the Ru/Mn-65/Al2O3 catalyst which is Mn content is 65 wt%.

2.2 Characterization

The prepared catalyst undergoes several characterization techniques to study its chemical and physical properties. The structure of the catalyst was determined by X-Ray Diffraction (XRD) using Cu Kα radiation (λ=1.54060 Å). Data was collected over the range of 2θ from 20 to 80° and analyzed by a PC interfaced to the diffractometer using software called Diffrac Plus. Field Emission Scanning Electron Microscopy (FESEM) analysis was measured using a Zeiss Supra 35VP FESEM with the energy of 15.0 kV couple with Energy Dispersive X-Ray (EDX) analyzer in order to determine the morphology and elemental composition of the catalyst. The sample was bombarded using an electron gun with a tungsten filament under 25 kV resolution to get the required magnification image. N2 adsorption/desorption isotherm (NA) analysis of the catalyst was obtained using Micromeritics ASAP 2010 volumetric adsorption analyzer at -196°C. Prior to the measurement, the calcined catalysts were degassed at 120°C overnight.

2.3 Catalytic Activity Measurement

The catalytic CO2methanation reaction was performed under atmospheric pressure in a fixed micro reactor and analyzed via online Fourier Transform Infra-Red (FTIR) Nicolet Avatar 670 DGTS. The supported catalyst was placed in the middle of the glass tube made of Pyrex glass with diameter of 10 mm and length of 520 mm. It was then secured with glass wool at both ends. The reaction gas mixture consisting of CO2, H2, N2, O2 (10/40/39/11) was passed continuously through the catalyst and was heated in an isothermal tube furnace. The total flow rate was set to 100 mL/min, while the weight hourly space velocity was kept fixed at 636 ml·g−1·h−1. The feed gas flow rate was adjusted with a mass flow controller and the reaction temperature was performed from 60 up to 300°C with the increment temperature rate of 5°C/min. Off line Gas Chromatography (GC) analysis (Hewlett Packard 6890 Series GC System) was done to determine the yield of CH4 gas due to the low sensitivity of FTIR spectroscopy towards the stretching band of CH4.
3.0 RESULTS AND DISCUSSION

3.1 Characterization

In this research, the content of catalyst was confirmed by Energy Dispersive X-Ray (EDX) analysis and is summarized in Table 1. The result was taken before the catalyst was calcined at 1000°C for 5 h. It can be seen that the ratio obtained from the EDX analysis was almost an equal value as stated in the catalyst ratio. Meanwhile, the physicochemical properties of the prepared catalysts are also listed in Table 1.

It is clearly observed that by promoting the ceria towards Ru/Mn/Al2O3 as based catalyst has a great influence on the BET surface area and average pore diameter. The BET surface area was increased remarkably from 8.52 to 47.65 m²/g, while pore diameter was decreased from 78.14 to 23.90 nm over Ru/Mn-65/Al2O3 and Ru/Mn/Ce-65/Al2O3 catalysts, respectively. This result indicates that the addition of Ce towards Ru/Mn/Al2O3 catalyst leads to the production of new active sites and hence increases its surface area.

Furthermore, the XRD analysis of Ru/Mn-65/Al2O3 revealed the rhombohedral (b) of Al2O3 2θ values of 35.13°(Ih0o), 43.329°(Ih0o), 57.410°(Ih0o), 25.550°(Ih0o), 68.089°(Ih0o), 52.475°(Ih0o), 37.323°(Ih0o) and 66.398°(Ih0o). It was transformed to the orthorhombic (o) Al2O3 at 2θ of 67.253°(1h0o), 34.522°(1h0o), 45.546°(1h0o) and 38.993°(1h0o) after the addition of ceria. It was probably due to the interstitials site that occurred in the structure of Ru/Mn-65/Al2O3 whereby some of the cerium atoms had occupied the space in the crystal lattice of Al2O3 thus changed the phase structure.

The peaks assigned to the tetragonal RuO2 remained similar at 2θ values of 54.965°(Ih0o) and 35.051°(1h17). However, the peak of RuO2 tetragonal phase at 28.124° (1h0o) was broader due to the sharing of peaks with face center cubic of CeO2 which was also observed at 28.548° (1h0o). Another two peaks of CeO2 was at 2θ of 56.344° (Ih0o) and in the enveloped of Al2O3 peaks at 2θ of 47.485° (Ih17).

Furthermore, the manganese oxide species was appeared in the form of tetragonal Mn3O4 over Ru/Mn-65/Al2O3 catalyst and detected at 2θ values of 61.872° (Ih0o). However, the pattern shows a very small peak which was hardly distinguished from the background noise. The overlapping of Mn3O4 diffraction peaks with those of the support peaks at 2θ of 36.466° (1h0o) also occurred. Conversely, manganese oxide species detected over Ru/Mn/Ce-65/Al2O3 catalyst was in the form of hexagonal Mn3O4 (2θ of 56.029°, 37.121° and 66.763°) and orthorhombic Mn2O3 (2θ of 32.921° and 55.141°).

FESEM images of Ru/Mn-65/Al2O3 and Ru/Mn/Ce-65/Al2O3 catalysts calcined at 1000°C are displayed in Figure 2. Generally, all the particles from both images are aggregated and agglomerated each other on the catalyst surface to form rough surface morphology. However, the catalyst with ceria addition (Figure 1b) showed slight different morphology which is like stag horn coral morphology. It was branches out to look like deer antlers on the surface of the. Such morphology will provide the space for the access of active metal components to attract CO2 and H2 molecules on the catalyst surface. Therefore, the surface area obtained from nitrogen adsorption analysis over Ru/Mn/Ce-65/Al2O3 catalyst is much higher than catalyst without ceria.

It can be suggested that the characteristic obtained from NA, FESEM and XRD analysis after promoting the ceria to Ru/Mn-65/Al2O3 as based catalyst would help the increasing of CO2methanation activity.

Table 1 Texture and composition analysis towards Ru/Mn/Al2O3 and Ru/Mn/Ce/Al2O3 catalysts prepared by wetness impregnation method and calcined at 1000°C

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Ce loading (wt.%)*</th>
<th>Mn loading (wt.%)*</th>
<th>Ru loading (wt.%)*</th>
<th>BET Surface Area (m²/g)</th>
<th>Average Pore Diameter (nm)</th>
<th>Cryst. Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/Mn-65/Al2O3</td>
<td>-</td>
<td>65</td>
<td>35</td>
<td>8.52</td>
<td>78.14</td>
<td>102</td>
</tr>
<tr>
<td>Ru/Mn/Ce-65/Al2O3</td>
<td>65</td>
<td>30</td>
<td>5</td>
<td>47.65</td>
<td>23.90</td>
<td>86</td>
</tr>
</tbody>
</table>

* Loading from Energy Dispersive X-Ray (EDX) analysis
*Crystallite Size data calculated by Scherer Equation

Figure 1 XRD diffractograms of a) Ru/Mn-65/Al2O3 and b) Ru/Mn/Ce-65/Al2O3 catalysts calcined at 1000°C for 5 h
3.2 Catalytic Performance

In this study, ceria was added to the Ru/Mn-65/Al2O3 catalysts to investigate the effect of ceria on catalytic CO2 performance. Prior to the start of testing, the prepared catalyst was preheated for half an hour at 100°C. From Table 2, the Ru/Mn-65/Al2O3 catalyst achieved maximum CO2 conversion at reaction temperature of 300°C with 51.10%. After the addition of ceria to the Ru/Mn-65/Al2O3 catalyst to form Ru/Mn/Ce-65/Al2O3, the activity was increased to 75.43% conversion at similar reaction temperature. It showed that the presence of ceria had improved the performance of Ru/Mn catalyst.

Table 2 Percentage conversion of CO2 from methanation reaction over various Ru/Mn/Al2O3 with or without ceria calcined at 1000°C for 5 h

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Reaction Temperature/ % CO2 Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100°C</td>
</tr>
<tr>
<td>Ru/Mn-65/Al2O3</td>
<td>6.81</td>
</tr>
<tr>
<td>Ru/Mn/Ce-65/Al2O3</td>
<td>10.53</td>
</tr>
</tbody>
</table>

3.2.1 Robustness Testing

Before the investigation to optimization of Ru/Mn/Ce-65/Al2O3 catalyst, the robustness of the prepared catalysts was studied. The robustness testing was performed on stream continuously for 20 h at reaction temperature of 300°C. Figure 3 shows the percentage of CO2 conversion as a function of reaction time over Ru/Mn/Ce-65/Al2O3 and Ru/Mn-65/Al2O3 catalysts.

It can be seen that the conversion of CO2 over Ru/Mn-65/Al2O3 increased for the first 10 h with maximum conversion of 78.32% and started to decrease gradually after that. In contrast, the catalyst modified with ceria, Ru/Mn/Ce-65/Al2O3 exhibited good stability under the present operating condition. For first hour reaction time, the Ru/Mn/Ce-65/Al2O3 catalyst managed to convert 98.83% CO2 and gradually increased until achieved 100% conversion at fifteen hours reaction time. After fifteen hour onwards, the catalyst was stable in terms of activity whereby the CO2 conversion was constant at 100%.

Therefore, the Ru/Mn/Ce-65/Al2O3 catalyst was categorized as a robust catalyst and was further optimized for several parameters such as different reduction temperatures, different calcination temperatures and ratios of the based/dopant catalyst. This process is important to obtain the best optimize condition towards the Ru/Mn/Ce-65/Al2O3 catalyst in order to get a great catalytic activity.

3.2.2 Effect of Reduction Pretreatments

In this section, catalytic performance of Ru/Mn/Ce-65/Al2O3 was studied by varying the pretreatment condition before start the CO2/H2 reaction. Prior to the start of testing, all the prepared catalysts were underwent air pretreatment at 100°C for 30 minutes. The reason to preheat the catalyst is to activate the catalyst as well as to remove the moisture in the catalyst. In this research, Ru/Mn/Ce-65/Al2O3 catalyst also underwent pretreatment in the presence of H2 gas (40 mL/min) at temperature of 100 or 300°C for half an hour which was under reduction condition. As such, the entire active sites on the surface of the catalyst will be reduced to lower oxidation number or to metallic state consequently increased its catalytic activity. The catalyst was also pretreated in the presence of O2 at 300°C as in Figure 4.
The catalyst with preheating at 100°C for 30 mins was already discussed in Section 3.2 above. The CO₂ conversion over this condition achieved 25.44% at reaction temperature of 200°C which was increased slightly compared to the catalyst without preheating (13.41%). Furthermore, the CO₂ conversion at similar reaction temperature was rose notably from 33.75 to 97.73% with the increasing of pretreatment temperature from 100 to 300°C in the presence of H₂. This result shows that the reduction pretreatment will cause the reorganization of the surface structure as claimed by Kim et al., where the C-O bond was weakened by the active oxygen on NiO, preferentially reacts with H₂. The surface carbon intermediate facilitated by NiO was then easily hydrogenated to produce methane. Meanwhile, pretreatment with O₂ just gave similar result to that preheated at 100°C.

### 3.2.3 Effect of Calcination Temperatures

To study the effect of calcination temperatures towards ceria catalyst in this research, the alumina supported ceria catalysts were calcined at 400, 900, 1000 and 1100°C. The trends of its catalytic performance are shown in Figure 5.

**Figure 5** Catalytic performance of CO₂ conversion from methanation reaction over Ru/Mn/Ce-65/Al₂O₃ catalyst calcined for 5 hours at different calcination temperatures

The CO₂ conversion of ceria impregnated by Ru/Mn/Al₂O₃ catalyst increased apparently with the increase of calcination temperatures until 1000°C and decreased back at 1100°C. It showed that the calcination temperature of 1100°C was not suitable where it seems that the catalyst was not stable and showed low CO₂ conversion at reaction temperature of 200°C (72.05%) compared to the catalyst that was calcined at 1000°C. The best calcination temperature of 1000°C over Ru/Mn/Ce-65/Al₂O₃ gave highest CO₂ conversion of 97.73% at reaction temperature of 200°C.

### 3.2.4 Effect of Ce Loading

In order to study the effect of ceria on catalytic performance, the CO₂ conversion was performed over Ru/Mn/Ce-65/Al₂O₃ catalyst by varying the ceria content from 60 to 85 wt%. The trend of CO₂ performance towards effect of ceria loading is depicted in Figure 6.

**Figure 6** Catalytic performance of CO₂ conversion from methanation reaction over Ru/Mn/Ce-65/Al₂O₃ catalyst calcined at 1000°C for 5 hours with various cerium loadings

It was clear that the presence of ceria had significant influence on the CO₂ conversion. The CO₂ conversion increased sharply from 49.43% to approximately 100% conversion at reaction temperature of 200°C with the ceria loading from 60 to 65 wt%. However, the promoting effect of CO₂ methanation would be unremarkable when further increase the ceria loading from 65 to 85 wt%. It clearly showed that an appropriate amount of ceria would increase the catalytic activity of the catalyst and surface basicity as well. Conversely, the excessive addition of ceria retarded the CO₂ conversion due to the enrichment of ceria on the catalyst surface which will cause the agglomeration to occur. Therefore, it can be concluded that the optimum loading for ceria content is 65 wt%.

### 3.2.5 Effect of Ceria Addition towards Methane Formation

Tables 3 shows the testing results of CO₂/H₂ methanation reaction over Ru/Mn/Al₂O₃ catalyst with or without ceria tested at optimum operating conditions. Both catalysts were calcined at 1000°C for 5 h and pretreated at 300°C for 30 mins in the presence of H₂. Overall, the CH₄ content was increased as temperature was increased.

It can be seen that, only 30.52% of methane was formed over Ru/Mn-65/Al₂O₃ catalyst at studied temperature of 200°C. However, the methane production was increased to 91.31% over 97.73% CO₂ conversion when ceria was added to the catalyst to form Ru/Mn/Ce-65/Al₂O₃ catalyst at similar reaction temperature. The other 6.42% of CO₂ conversion was probably formed the product of CO.
### Table 3  Methane formation over various Ru/Mn/Al₂O₃ with or without ceria calcined at 1000°C for 5 h, pretreated at 300°C for 30 mins in the presence of H₂

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Reaction Temperature</th>
<th>% Conversion of CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100°C</td>
<td>200°C</td>
</tr>
<tr>
<td>Ru/Mn-65/Al₂O₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru/Mn/Ce-65/Al₂O₃</td>
<td>8.7</td>
<td>91.31</td>
</tr>
</tbody>
</table>

#### 4.0 CONCLUSION

The modification of the Ru/Mn-65/Al₂O₃ catalyst by adding the ceria as a based could change the structure of the catalyst. The phase transformation of crystalline to polycrystalline state cause the increasing of catalyst surface area, giving smaller particles size, reducing the average pore diameter of the catalyst as well as change the morphology to staghorn coral like morphology. Those properties would increase the catalytic activity over Ru/Mn/Al₂O₃ catalyst to 97.73% as well as 91.31% of methane was formed from the reaction at reaction temperature 200°C. The catalyst promoted by ceria exhibited excellent stability for 20 h on stream without deteriorate. The operating condition of 65 wt% of ceria, calcined at 1000°C for 5 h, and pretreated with H₂ at 300°C for 30 mins would be the ideal conditions for the catalytic methanation over Ru/Mn/Ce-65/Al₂O₃ catalyst.

### Acknowledgement

The authors are gratefully acknowledged to the Ministry of Science, Technology and Innovation, Malaysia for E-Science Fund Vote 4S082, Ministry of Higher Education, Malaysia for GUP Fund vote 04H97 and UniversitiTeknologi Malaysia for financial support.

### References