In Malaysia, urban dwellers have rapidly increased and at the same time, claims for certain types of products have been increased to meet the demands of the present society. Modern societies rely heavily on vehicles like cars, trucks and trains. The release of the vehicle is depend primarily on the burning of fossil fuels, thereby contributing to the dominant greenhouse gases (CO₂, SO₂, NOₓ) emitted in the air either inside or around the world. Carbon dioxide is the most important greenhouse gas generated by transport activities and it affects the global warming if its emission is not been controlled or reduced, as investigated by Yusof et al. (2010). Carbon dioxide must be eliminated to prevent or reduce harmful gases that released to the environment. This will reduce problem such as acid rain, ozone reduction, or greenhouse gases. Therefore, appropriate methods are needed to overcome this problem. Recently, alternative methods have been developed, such as the conversion of CO₂ catalysts through the methanation reaction. The catalytic methanation reaction refers to the process of converting carbon monoxide and carbon dioxide from the gas stream to produce methane using catalyst (Mills and Fred, 1974). This will eliminate toxic carbon dioxide and produce methane at the same time. It is also economically viable because the catalyst is recyclable and ecologically correct, as it does not release toxic gases into the air during the reaction. As the catalytic methanation reaction has been proven to provide an excellent performance of converting CO₂ in the simulated natural gas in the previous study using Ru/Mn/Co-Al₂O₃ (Rosid et al., 2018a), therefore, the present study was steered in order to study the effect of based cerium, ruthenium and catalyst loading using double reactor towards catalytic activity and physicochemical properties at low reaction temperature.

### EXPERIMENTAL

#### Materials

Chemicals used in this research were cerium(III) nitrate hexahydrate (Sigma Aldrich Chemical), ruthenium(III) chloride (Molekula), aluminium oxide (MERCK Eurolab), and manganese nitrate tetrahydrate (Sigma Aldrich Chemical).

#### Synthesis of Ru/Mn/Co catalyst

Cerium salt was weighed (5g) in a beaker together with manganese and ruthenium according to the desired ratio and were dissolved in small amount of distilled water. Then, the solutions were mixed together and stirred continuously by magnetic bar for 30 minutes at room temperature to homogenize the mixture. Then, alumina beads with diameter of 3 mm were immersed into the catalysts solution for 20 minutes and the supported catalysts were transferred onto evaporating dish with glass wool on it. They were then aged in an oven at 80–90°C for 24 hours to remove water and allow good coating of the metal on the surface of the supported catalysts. They were then calcined in the furnace at 400°C for 5 hours under ambient atmosphere using a ramp rate of 10°C/min to eliminate
all the impurities, metal precursors and excess of water. The steps were repeated and applied for all different ratios of catalysts.

**Catalytic activity using FTIR, GC, and HPLC**

The reaction gas mixture consisting of CO₂ and H₂ in a 1:4 molar ratio was continuously passed through the catalyst and heated in an isothermal tubular furnace. The product stream was collected on a FTIR sample cell with attached KBr windows and scanned using the Nicolet Avatar 370 DTGS FTIR spectrophotometer. Gaseous products were periodically analyzed by gas chromatography to determine the formation of methane from CO₂ conversion reaction. The Hewlett Packard 6890 Series gas chromatography system via flame ionization detector (FID) was set at initial temperature of 40°C for 7 minutes and at injection temperature of 150°C. The presence of methanol content was observed by HPLC (Rezex ROA organics) using a column of 300 mm × 7.8 mm ID with Refractive Index (RI) detector with 0.005 N sulfuric acid as an eluent.

**Characterization**

In XRD analysis, the sample was manually crushed into fine powder and then placed into the sample holder. The XRD pattern was recorded by the D5000 Siemens Crystalloflex Diffractometer with Cu Kα radiation (λ=1.54060 Å). The spectrometer of XPS was flushed by using argon gas at 6×10⁻⁶ Torr before putting the sample for spectrum recording to maintain sample surface integrity. Before analyzing the sample, the spectrometer was calibrated using a clean argentum crucible by assuming that the binding energy for Ag 3d₅/₂/₂ was 368.25 eV. From the spectrum, the peak for C 1s was obtained at binding energy of 284.5 eV, which could be taken as the second reference. Dried powder sample was analyzed by Kratos surface analysis spectrometer XSAM HS instrument using MgKα (1253.6 eV) as the X-ray source.

**RESULTS AND DISCUSSION**

**Characterization of catalyst**

Different Ce loadings revealed almost similar diffractograms, as shown in Fig. 1, where the peak was more intense and sharper, with high crystallinity. As could be observed, at ratio of 55% and 65%, both showed the existence of RuO₂ species with tetragonal phase. The phases detected at 55% of Ce loading were CeO₂ (cubic), Al₂O₃ (cubic), MnO₂ (tetragonal), Al₂O₃ (rhombohedral) and RuO₂ (tetragonal). CeO₂ with cubic phase was revealed at 2θ values of 28.48° (I100), 47.43° (I101), 56.40° (I111), 76.20° (I100) and 79.04° (I10). Meanwhile, cubic Al₂O₃ was detected at 2θ values of 67.17° (I100), 45.43° (I100), 36.82° (I100) and 60.45° (I10). The overlapping peaks of MnO₂ with tetragonal phase were observed at 2θ value of 28.48° (I100), 36.87° (I111), 56.54° (I101) and 70.09° (I10). According to Wang et al. (2012), the rhombohedral of Al₂O₃ was detected at 2θ values of 67.13° (I100), 43.31° (I101), 57.46° (I101), 25.58° (I100), and 52.53° (I10). As reported by Matori et al. (2012), the rhombohedral of Al₂O₃ was observed at calcination temperature above 880°C. The rhombohedral α-Al₂O₃ is the stable phase through the nucleation and the crystallite growth process. Therefore, it was capable in increasing the particle size which then causing in a decrease of the surface area. In consequence, it would lower the catalytic activity. Similar observation was also detected for the catalyst that calcined at 1000°C for ratio of 65%. However, in the diffractogram for ratio of 60%, only Al₂O₃ cubic, CeO₂ cubic and MnO₂ tetragonal phase were detected. The Al₂O₃ cubic was revealed at 2θ values of 67.13° (I100), 45.60° (I101), and 36.46° (I101), while the peak for cerium oxide cubic has been assigned at 2θ values of 28.51° (I100), 47.41° (I101), 56.43° (I101), 33.13° (I100), 76.36° (I100) and 79.02° (I10). Meanwhile, MnO₂ with tetragonal phase was observed at 2θ values of 28.56° (I100), 36.98° (I101) and 56.60° (I101).

XPS was used to determine the composition of the elements in the catalyst and the chemical state of the element. In this study, the charge of the specimen, the C 1s line (284.50 eV) was used as the standard. The peak of Ru was not detected in Ru/Mn/Ce (5:35:60)/Al₂O₃ and this result was supported with XRD, in which no peak of Ru was observed. Fig. 2 displays the wide scan of the XPS spectrum based on the existence of different types of elements in the Ru/Mn/Ce (5:35:60)/Al₂O₃ catalyst sample calcined at 1000°C.

The atomic concentration of Ce detected by XPS was low (<0.20%), indicating the partial surface encapsulation of Ce and slow formation of oxygen vacancy on the alumina support, as also observed by Luches and Valeri (2015). According to XPS NIST database, the deconvolution peaks were belonged to Ce4⁺ with the formation of CeO₂ compound, as shown in Fig. 3. Typically, Ce 3d XPS core-level spectra exhibited three-lobed envelopes (around 879–890 eV, 895–910 eV and approximately 916 eV). The peak of cerium was
decomposed into six components to form two doublets. The first doublet was corresponded to Ce 3d5/2 (Eb = 882.16 eV) and Ce 3d3/2 (Eb = 887.09 eV). The second doublet was corresponded to Ce 3d5/2 (Eb = 900.89 eV) and Ce 3d3/2 (Eb = 904.15 eV), while the third doublet at Ce 3d5/2 (Eb = 907.50 eV) and Ce 3d3/2 (Eb = 884.41 eV) were attributed to cerium under its oxidized form. As could be seen, there was no systematic evolution in the positions of different peaks in which suggesting that the presence of manganese oxides did not alter the cerium chemical environments as it formed a synergistic interaction between manganese and ceria species as discussed by Liu et al. (2015). This finding was supported with XRD data where CeO2 was observed in the diffractogram (Fig. 1).

XPS spectra for Mn 2p were consisted of two doublets as shown in Fig. 4, which were Mn 2p1/2 and 2p3/2. According to literature, the binding energy, Eb of Mn 2p1/2 in pure manganese oxides could be found at 641.2 eV (Mn2+), 641.8 eV (Mn3+), and 642.1 eV (Mn4+), respectively. In this study, a compound with MnO2: (Mn10+) was observed at peak Eb value of 642.26 eV. This was in a good agreement with XRD analysis which MnO2 species was observed in the diffractogram. Deconvolution of Mn 2p produced 2 peaks at Eb value of 642.26 eV and 644.49 eV for Mn 2p1/2, which were attributed to MnO2 species. Meanwhile for Mn 2p3/2, 2 peaks at Eb value of 654.36 eV and 656.32 eV were also attributed to MnO2. The other two peaks with binding energy at Eb value of 641.82 eV and 653.05 eV were assigned to Mn2O3 species. However, this species was not observed in XRD analysis, which suggested that this was not an active species.

The BET analysis showed that when cerium loading was increased to 65%, the surface area was decreased from 50.95 m2/g to 32.72 m2/g due to the removal of pores and the formation of dense solid as been discussed by Rosid et al. (2018). Therefore, it could be concluded that high surface area was important in catalytic activity since it would provide more active surfaces for catalytic interaction. The BJH pore size distribution indicated a pore diameter of around 75-120 nm and this was supported with smaller hysteresis. The presence of a single peak from the graph of pore size distribution in Fig. 5 was indicated to the presence of pores in the catalyst sample. The plot was corresponded to the Type IV isotherm and H3 hysteresis which consisted of aggregated or agglomerated particle in forming non-uniform slit shaped pores for the adsorption of CO2 and H2 gases as investigated by Thommes et al. (2015).

**Effect of various metal oxide based loadings**

The potential catalyst, Ru/Mn/Ce-Al2O3 was optimized using different cerium based loadings to observe its effect on the catalytic activity. The ratios of 50-85 wt% of cerium oxide catalysts were selected. Fig. 6 showed that the trend plots of catalytic performance when the Ce content was increased to 60%, the conversion of CO2 was increased, but it was decreased as the Ce content was up to 85%. Perhaps, this was due to the blocking of surface active sites and pore structure by excessive loading of Ce, promoting the particle to nucleate as well as inhibiting the growth of crystal (Rosid et al., 2019). Therefore, the optimum cerium loading was 60%, which gave 100% CO2 conversion.

**Effect of various ruthenium loadings**

The catalytic activities of potential catalyst with different ruthenium loadings (5 wt%, 10 wt%, and 15 wt%) were investigated. CO2 conversion for each catalyst was started to increase significantly at 250°C reaction temperature. Fig. 7 showed that the CO2 conversion...
was decreased as the ruthenium loading was increased. As a result, the optimum ruthenium loadings to achieve higher CO₂ conversion was 5 wt%. This behavior might be due to an excessive distribution of ruthenium content on the support surface as suggested by Zhang et al. (2012). This finding was also in an agreement with a study conducted by Rosid et al., (2015), which stated that the addition of 5 wt% of ruthenium to lanthanum oxide catalyst could enhance the catalytic activity by achieving almost 100% of CO₂ conversion.

**Catalyst testing on CO₂ methanation reaction using double reactors**

In this section, the Ru/Mn/Co (5:35:60)-Al₂O₃ catalyst was tested using two reactors instead of using one reactor, as in previous section. This testing was conducted using two isothermal furnaces connected in series. The catalyst loading was doubled in this process to examine the conversion percentage when more catalysts were utilized. Using two reactors in the catalytic activity process was also relevant in providing more time for the reaction to occur in order to maximize conversion of CO₂. This method was also suitable for industrial application. Fig. 8 showed that the percentage of CO₂ conversion over Ru/Mn/Co (5:35:60)-Al₂O₃ catalyst calcined at 1000°C by double reactor was 95.83% at 350°C reaction temperature. The performance of the catalyst was slightly lower compared to single reactor over the same catalyst that achieved 100% at the same reaction temperature. The findings by Li et al., (2014) were in agreement with our results that stated the decrease of CO₂ conversion in the second reactor might be caused by the formation of water in the first reactor at low temperature which blocked the catalyst surface during reaction at the first reactor.

**Detection of methanol by high performance liquid chromatography (HPLC)**

The methane formation which detected by GC using a single reactor for this potential catalyst was far from the value of CO₂ conversion. Therefore, HPLC tests were conducted to confirm the presence of methanol as a side product. The HPLC analysis illustrated that the compound of interest was eluted at retention time of 20 min for standard methanol. When the sample was injected, peaks were started to appear at 20 min of retention and assigned to methanol compound as it was compatible with standard methanol (not shown).

**CONCLUSION**

The potential Ru/Mn/Co (5:35:60)-Al₂O₃ catalysts with various based cerium, ruthenium, and catalyst loadings have shown an effect towards catalytic activity and physicochemical properties. The percentages of CO₂ conversion for Ru/Mn/Co (5:40:55)-Al₂O₃, Ru/Mn/Co (5:45:55)-Al₂O₃, and Ru/Mn/Co (5:50:55)-Al₂O₃ were 74.53%, 100% and 96.12%, respectively at 400°C of reaction temperature. The products of this reaction were confirmed to be H₂O, CH₄ and CH₃OH. The XRD analysis revealed that the active species in the potential catalyst were CeO₂ and MnO₂, meanwhile corundum rhombohedral Al₂O₃ was assigned as an inhibitor species at 55% and 65% cerium loading. The presence of active species was supported with XPS analysis and BET analysis showed that the surface area was lower for 55% and 65% with 27.23 m²/g and 32.72 m²/g, respectively.

**ACKNOWLEDGEMENT**

The authors would like to thank to Universiti Sultan Zainal Abidin, Universiti Teknologi Malaysia and Ministry of Higher Education (MOHE), Malaysia for financial support.

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