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CHARACTERISTIC OF PRASEODYMIUM OXIDE DOPED MANGANESE/RUTHENIUM CATALYST IN METHANATION: EFFECT CALCINATION TEMPERATURE

Salmiah Jamal Mat Rosid[1]*, Susilawati Toemen[2], Wan Azelee Wan Abu Bakar[2], Sarina Mat Rosid[3], Wan Nazwanie Wan Abdullah[4], Siti Maisarah Aziz[1]

[1]*Unisza Science and Medicine Foundation Centre, Universiti Sultan Zainal Abidin, Gong Badak Campus, 21300 Kuala Nerus, Terengganu, Malaysia*
[2]*Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia*
[3]*Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia*
[4]*School of Chemical Science, Universiti Sains Malaysia, 11800 Minden, Pulau Pinang, Malaysia*

**Corresponding author: salmiahjamal@unisza.edu.my*

Abstract

Lanthanide element in the methanation reaction gives an excellent catalytic performance at low reaction temperature. Praseodymium is one of lanthanide element and was chosen due to its properties which are thermally stable and provide excess of oxygen in the oxide lattice. Therefore, a catalyst of Ru/Mn/Pr (5:30:65)/Al_2O_3 (RMP, 5:30:65/Al_2O_3) was prepared via wetness impregnation method and the effect of calcination temperature on the catalyst performance was investigated using FTIR analysis. The RMP/Al_2O_3 catalyst calcined at 800 °C was chosen as an excel catalyst with CO_2 conversion of 96.9% and CH_4 formation of 45.1% at 350 °C reaction temperature. From the EDX mapping, it can be observed that the distribution of all element is homogeneous at 800 °C and 900 °C except Ru, O and Al at 1000 °C calcination temperature. The image from FESEM also shows the presence of some crystal shape on the catalyst surface. From the FTIR analysis, the peak stretching and bending mode of O-H bond decreased when the calcination temperature increased.

Keywords: calcination temperature, methanation, morphology, praseodymium

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Introduction

Demanding industry of natural gas has led to air pollution by emission of CO_2 gas to the environment. Therefore, it is important to develop technologies that enable the use of fossil fuels while reducing greenhouse gas emissions. Methanation reaction is one of the green technologies that convert waste to wealth which is CO_2 to CH_4. However, for the implement in an industry, low reaction temperature is required. Recent study shows that lanthanide element gives an excellent catalytic performance in methanation at low reaction temperature (Asif Iqbal et al.,2020, Rosid et al., 2019).

Despite, to give an excellent catalytic performance, a few parameters will affect the catalytic activity especially calcination temperature. According to previous studies, calcination temperature is the most important parameter that has a significant effect on catalytic activity, texture, structure, phase, and catalytic properties (Rosid et al., 2017, Zamani et al., 2019, Wu et al., 2020). It is believed that an increase in calcination temperature also promotes agglomeration of catalyst particles, thus affecting crystallite size and surface area (Branco et al., 2020, Md Ali et al., 2017).

Therefore, praseodymium was chosen due to its properties which are thermally stable and provide excess of oxygen in the oxide lattice (Ferro, 2011). In this study, a trimetallic oxide catalyst, RMP

(5:30:65)/Al_2O_3 catalyst was synthesized by wetness impregnation method and the influence of calcination temperature towards characteristic catalytic activity structure relation was studied.

Methods

Preparation of catalyst

A catalyst with ratio 5:30:60 was prepared using 5 g of $Pr(NO_3)_3.6H_2O$ and dissolved with minimum amount of distilled water to be ratio 60% wt. Then, $MnNO_3.4H_2O$ solution and $RuCl_3.H_2O$ solution was added based on ratio 35% wt and 5% wt respectively. The catalyst solution was stirred for 30 minutes and then doped with alumina beads. The catalyst was then dried in the oven at 90 °C overnight, followed by calcination at 400 °C,700 °C, 800 ºC,900 °C and 1000 °C for 5 hours.

Catalytic activity measurement

The catalytic reaction of CO_2 methanation was performed under atmospheric pressure in a fixed micro reactor and analyzed via online Fourier transform infrared. The mixed gas composition of CO_2 and H_2 in the reactor was similar to the composition of crude natural gas with a molar ratio of 1:4 each at a flow rate of CO_2/H_2 = 50.00 cm^3/min. The FTIR spectrum was recorded with a resolution of 4 cm^{-1} in the range 4000-450 cm^{-1}, and the signal-to-noise ratio improved after 5 scans. Equation 1 shows the percentage of the CO_2 conversion calculation. Catalyst measurement data were collected according to the peak area of the reaction gas within the wavenumber range, as shown in Table 1.

$$\%\text{ of } CO_2 \text{ Conversion} = \frac{\text{Peak Area of } CO_2 \text{ calibration} - \text{Peak Area of } CO_2 \text{ conversion}}{\text{Peak area of } CO_2 \text{ calibration}} \times 100\% \qquad (1)$$

Table 1. Wavenumber of CO_2, CO, and CH_4 in FTIR spectrum

	Wavenumber (cm^{-1})	
Component of gases	**Stretching mode**	**Deformation mode**
CO	2100 - 2200	-
CO_2	2397 - 2275	800 - 600
CH_4	3200 - 2850	1400 - 1300

Characterization of catalyst

Morphological characterization with a Field Emission Scanning Electron Microscope (FESEM) was performed using the Zeiss Supra 35VP brand in combination with an Electron Dispersive X-ray (EDX) analyzer. The Thermogravimetric analysis - Differential Thermal Analysis (TGA-DTA) analysis was done by thermal analyzer TGA-SDTA 851 Mettler Toledo from temperature of 60 to 900 °C with flows rate of nitrogen gas 50 µL/ min. Functional group was observed using Fourier Transform Infrared Spectroscopy (FTIR) Spectrometer Nicolet Avatar 370 DTGS and transference film was prepared using potassium bromide (KBr) pellet with ratio of 1:100.

Result and Discussion

Effect of Calcination Temperature

The catalyst for RMP/Al_2O_3 was investigated for the effect of calcination temperature on catalytic performance using in-situ FTIR analysis. Figure 1 shows a trend plot of catalytic activity for RMP/Al_2O_3.

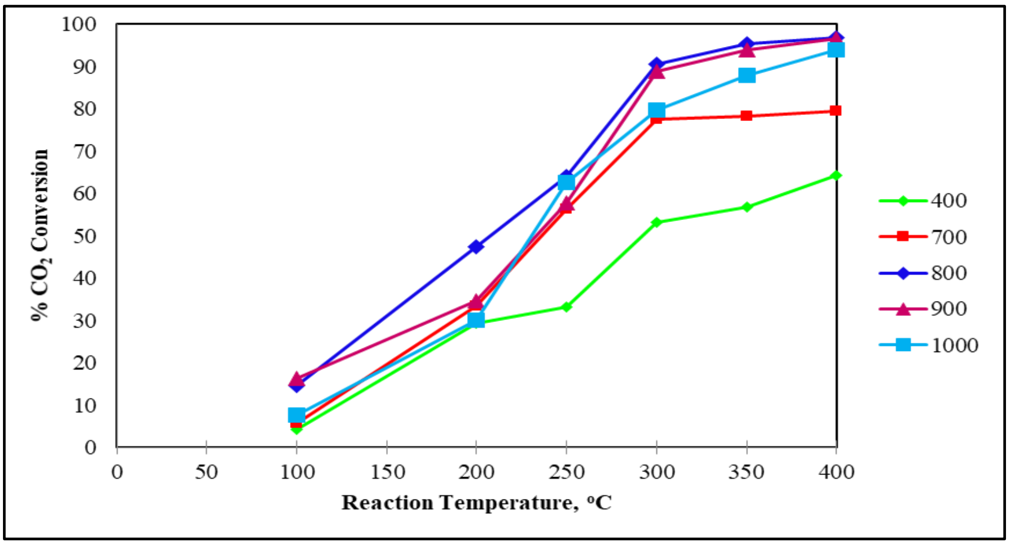

Figure 1. Trend plot of CO_2 conversion for RMP/Al_2O_3 catalyst at various calcination temperatures

The figure showed that the CO_2 conversion increased when reaction temperatures were increased until 400 °C. Meanwhile, increasing calcination temperature also give effect to the catalytic performance by increment conversion of CO_2 from 64.3% at 400 °C to 96.90% at 800 °C. This might due to at low calcination temperature is not conducive to the formation of active species on the catalyst surface. As calcination temperature rises also, Pr^{3+} and Mn^{4+} species may be easier to dissolve into the Al_2O_3 lattice to form stable mixed oxide. However, a further increase in the calcination temperature up to 1000 °C calcination temperature, the slight decreased of CO_2 conversion was obtained by 94.1%. This might due to occurrence of sintering migration atom from the rare earth element which caused the reduce active surface area and formation of large-grain crystalline Pr-O (Rostrup-Niclsen *et al.*, (2007)). Therefore, RMP/Al_2O_3 calcined at 800 °C was chosen as an excel catalyst for giving higher CO_2 conversion.

FESEM-EDX Analysis

Figure 2 shows the FESEM-EDX mapping profile of RMP/Al_2O_3 catalysts calcined at temperatures of 800 °C, 900 °C, and 1000 ° C with 50 000 magnification. At calcination temperatures of 800 °C and 900 °C, all distribution of active elements, Al, Pr, Mn, and Ru were homogeneous and well distributed as can be seen in EDX mapping. Moreover, the FESEM image at 800 °C showed some of small crystal shape particle on the surface which might belong to praseodymium oxide (Ferro, 2011). Similar morphology was observed at 900 °C, but with a larger crystal shape particle size. Meanwhile, the FESEM morphology at a temperature of 1000 °C shows the abundance of larger crystallite distribution. This may due to high calcination temperature of 1000 °C has caused an increase in the amount of praseodymium on the surface of alumina (Schmitz *et al*., 1993). The formation of larger crystallite leads to the decreased catalytic activity as suggested by Sehested, (2003) which support the result in Figure 1. In contrast, the Ru and Al elements are not homogenized and form some clusters. This clusters might contribute to the decreased of catalytic activity at 1000 °C calcination temperature.

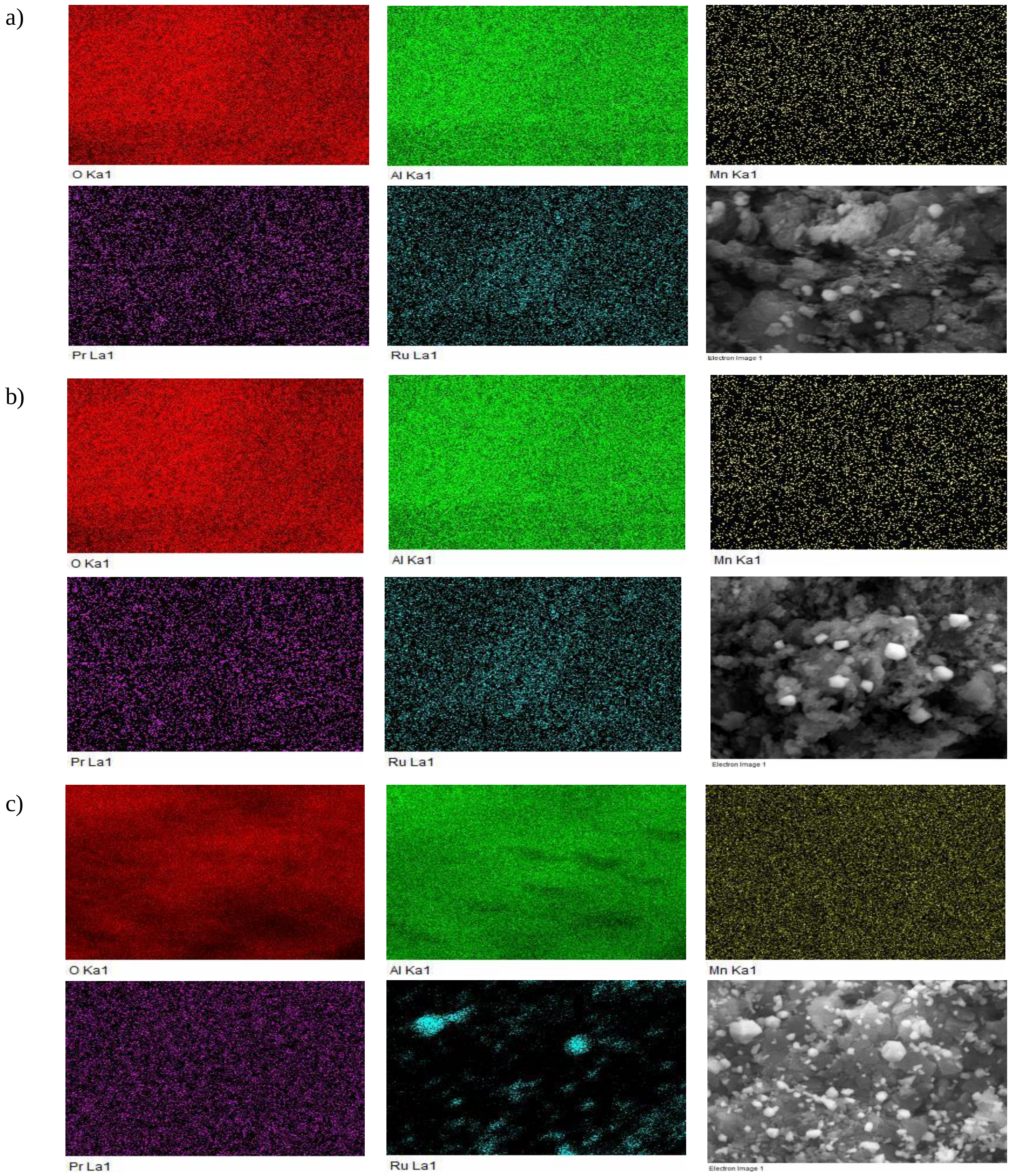

Figure 2. EDX mapping profile and FESEM image of RMP/Al_2O_3 catalyst calcined at a) 800 °C, b) 900 °C and c) 1000 °C with 50 0000 magnification

Thermogravimetric (TGA-DTA) Analysis

The weight loss to decompose completely is an important analysis to determine the minimum temperature for catalyst to be thermally stable by calcination process. The TGA-DTA thermogram was depicted in Figure 3.

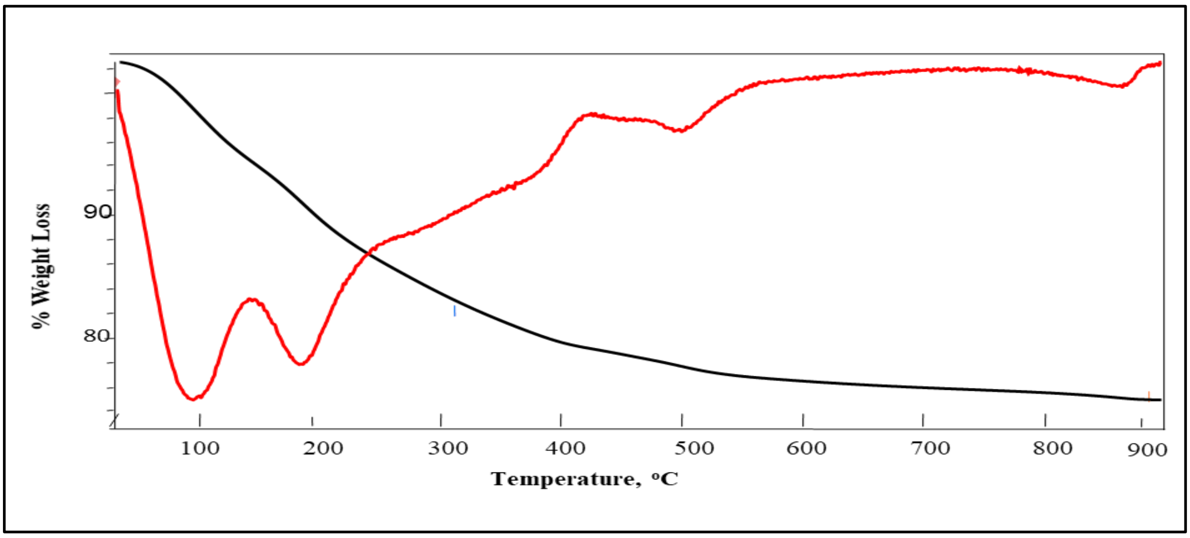

Figure 3. TGA-DTA thermogram of fresh RMP/Al_2O_3 catalyst

From the figure, there are four region of weight loss which the first region 60 °C to 150 °C was due to the removal of physiosorbed water. This was supported with an intense endothermic DTA curve which agreed for heat desorption of water as also observed by Rahemi *et al.*, (2013). The second region representing the nitrate decomposition compound with a broad endothermic peak at 160-260 °C (Savva *et al.*, 2008). The weight loss at 320-430 °C was due to decompose of bonded water from the alumina which was also reported by Rahemi *et al.*, (2013). The final mass loss region from 430 °C to 900 °C is assigned to the degraded hydroxyl molecule with an endothermic DTA curve at 500 °C. The Pr_2O_3 species are known to absorb carbon dioxide and water from the air, as described by Anderson and Gallagher (1963). Therefore, mass loss is caused by the release of bound water or carbon dioxide from the surface of the amorphous catalyst. The small endothermic DTA curve at 860 °C showed the formation of pure oxide phase doped catalyst through morphological and structural modifications (Bakar *et al.*, 2012). Thus, it can be proposed that stable metal oxide was attainable only after calcination temperature of 900 °C. Therefore, the calcination temperature above 900 °C was suitable to thermally stabilize the catalysts as also observed by Parathasarathi *et al.,* (2000).

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The existence of functional groups in the catalyst was identified using FTIR analysis at 800 °C, 900 °C and 1000 °C calcination temperature as depicted in Figure 4.

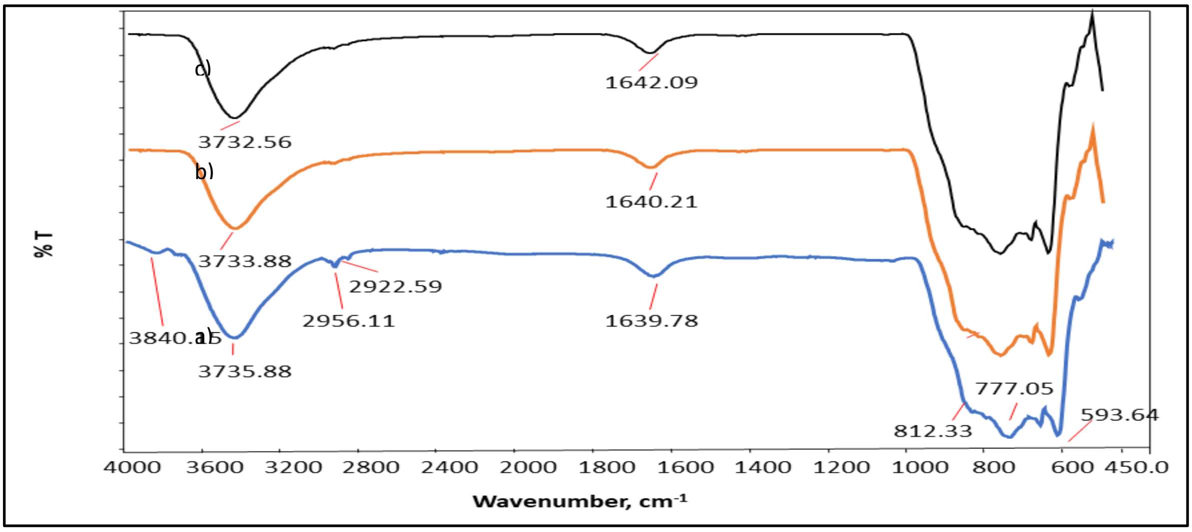

Figure 4. FTIR spectra of RMP/Al_2O_3 catalyst calcined for 5 hours at a) 800 °C, b) 900 °C, and c) 1000 °C

The spectrum shows that in the RMP/Al_2O_3 catalyst calcined at 800 °C, OH stretch bands were observed at 3735.88- 3732.56 cm^{-1} and 2920 cm^{-1} suggested to water molecules absorbed on the surface of the catalyst. As Coates (1998) suggests, the vibration of O-H bonds is widened by the expansion and contraction absorption of hydrogen bonds. In addition, the absorption band of 1642.19-1639.78 cm^{-1} was due to the bending mode of the adsorbed water molecules. Alternatively, an absorption band of 593.64-812.23 cm^{-1} was observed as the presence of Pr-O lattice vibration stretching mode (Abdullah et al., 2012). As the calcination temperature increased, the peak mode of O-H bond elongation and bending decreased. This might due to when calcination temperature increased, the absorption water molecule on the catalyst surface was decreased.

Conclusion

RMP/Al_2O_3 catalyst calcined at 800 °C was chosen as an excel catalyst with 96.9% CO_2 conversion at 400 °C reaction temperature. EDX mapping at 800 °C shows that distribution of element O, Al, Mn, Pr and Ru were highly homogeneous which contribute the high catalytic activity. The FESEM image shows the presence of crystal structure which may assist the catalytic activity. TGA thermogram revealed that the minimum temperature is 600 °C for the catalyst be thermally stable. Meanwhile, FTIR spectra exhibited that when calcination temperature increased, the peak O-H bonding decreased.

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