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Characterization and modelling optimization on methanation activity using Box-Behnken design through cerium doped catalysts

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ABSTRACT

Catalytic methanation reaction has been a promising technique for the conversion of CO_2 to valuable fuel product, CH_4 and thus reduces the emission of CO_2 to the environment. Many catalysts have been investigated by this method yet some carbon depositions have occurred during reaction which leading to low conversion rate of CO_2 to CH_4. Therefore, cerium catalyst has been applied in this study for the investigation of catalytic activity utilizing response surface methodology (RSM) method (Box-Behnken Design) in order to achieve the highest CO_2 conversion. The potential trimetallic oxide catalyst of Ru/Mn/Ce (5:35:60)/Al_2O_3 was chosen and the experimental parameters used were calcination temperature of 600–800 °C, ratio based loadings of 60–80 wt%, and catalyst dosage of 3–7 g with CO_2 conversion to CH_4 as a respond. The RSM optimum parameter of calcination temperature of 697.47 °C, ratio of 60.38% and catalyst dosage 6.94 g was tested. At these conditions, the results were verified experimentally (99.98% CO_2 conversion), which was accurately close to the predicted value (100% CO_2 conversion). Ru/Mn/Ce (5:35:60)/Al_2O_3 catalyst revealed the active species of CeO_2 in XRD analysis with oxidation state Ce^{4+} as supported by ESR analysis. When the calcination temperature was increased, the surface area decreases as observed in nitrogen adsorption supported with larger particle size as shown in FESEM. The reducibility of cerium catalyst was started at lower temperature.

1. Introduction

Natural gas has received a great demand for the industry and daily activities which at the same time to achieve a reduction of greenhouse gases [Pan et al., 2017, Osazuwa and Cheng, 2017]. However, Malaysia's natural gas producing sour natural gas which consists of polluted gaseous such as CO_2 which accumulate in the atmosphere when it was released to the environment [Pan et al., 2017]. Therefore, green technology is necessary to identify and solve the issues of energy and environmental gradually for all over the world as stated by Islam et al (2009).

Thus, to produce a clean burning and environmental friendly of natural gas [Dong et al., 2017, Kakaee et al., 2014], a gas sweetening process is needed to remove of acid gases such as CO_2, H_2S and other sulphur components [Zhang et al., 2017, Sadegh et al., 2017]. The most promising method for removing higher content of CO_2 from natural gas is catalytic methanation. This methanation process has been widely explored in terms of catalysts and condition processes. For the natural gas purification, the important process is conversion of carbon dioxide to methane by using hydrogen gas as shown in Equation (1.1) below [Toemen et al., 2017].

$$CO_2 + 4H_2 \xrightarrow{\text{Catalyst}} CH_4 + 2H_2O \qquad (1.1)$$

The most important criteria for the methanation catalyst are thermal stability, coke formation, fouling, and basicity. Thermal stability is an important to make sure that the reaction temperature is low because it affects the equilibrium state of the reaction and the catalyst life decreases if it is too high. The formation of coke will blocks the reactants from reaching the active site and the fouling are formed by the reaction forming a product which when covered on the active site. Besides that, the catalyst selection for CO_2 methanation reaction should have higher basicity and high surface area with small particle sizes dispersed on the catalyst surface. The dispersion may help to stabilize the active species [Toemen et al., 2017].

However among other catalysts studied, the deactivation of catalyst always occurs due to carbon deposition on the catalyst surface. Therefore, it is necessary to develop catalysts that are

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highly efficient and stable against sintering and carbon deposition. Up to date, only a few researchers have investigated the lanthanide oxide as based catalyst towards methanation reaction. Based on the Du et al., 2007 studies, the using of lanthanide elements can affect the physical and chemical characteristic of the based catalyst. One of the elements that have been investigated was cerium. This is due to its high specific surface area and strong redox ability. It also possesses a higher degree of stabilization upon ionization [Biinzli and Piguet, 2005]. Rao and Mishra, 2003 also stated that a highly basic catalyst like cerium oxide can enhance the CO_2 adsorption and chemisorption on the catalyst surface. Its excellent redox properties resulted in a very fast reduction of Ce^{4+}/Ce^{3+}, which attributed to the formation of oxygen vacancies on the surface.

Rynkowski et al. (2000) had investigated the activity of Ru/Al_2O_3 and $Ru/CeO_2/Al_2O_3$ catalysts for methanation reaction with 72% and 76% of CO_2 conversion respectively. The catalysts were active at reaction temperature above 200 °C, showing a very high selectivity to methane which close to 100%.and a relatively high stability for 340 h with reduction to about 80% from the initial one.

Previously, Wan Abu Bakar et al., 2010 had investigated Ru/Mn (25:75)/Al_2O_3 which improve catalytic performance. The CO_2 conversion was increased from 17.18% at 200 °C to 89.01% at 400 °C. From the XRD, it can be observed that Mn and Ru enhance the catalytic activity because H_2 and CO_2 are easily chemisorbed and activated on these surfaces. Toemen et al. (2014) also has investigated trimetallic ceria catalyst calcined at 1000 °C with 97.73% CO_2 conversion and 91.31% CH_4 at 200 °C reaction temperature for fuel gases. However, higher based loading and calcination temperature was not cost effective in industrial application.

Therefore, Mat Rosid et al. (2015) has studied Ru/Mn/Ce (5:35:60)/Al_2O_3 catalyst calcined at 700 °C with 100% CO_2 conversion and 80% CH_4 formation. This paper has continued focuses on the optimization of Ru/Mn/Ce (5:35:60)/Al_2O_3 catalyst by Box-Behnken design with three dependable parameter. The optimum condition was studied to improve the catalyst performance during methanation reaction.

2. Experimental

2.1. Preparation of Ru/Mn/Ce(5:35:60)/Al_2O_3 by incipient wetness method

The base metal precursor was prepared by dissolving cerium (III) nitrate hexahydrate (5.00 g) with distilled water and stirred. Then, the manganese nitrate tetrahydrate and ruthenium (III) chloride salt were dissolved with distilled water. These solutions were mixed and stirred continuously by magnetic bar for 30 min at room temperature to homogenize the mixture. Then, alumina beads with diameter of 3 mm was immersed into the catalysts solution for 20 min before transferred onto evaporating dish with glass wool on it. Then the catalyst was aging inside an oven at 80–90 °C for 24 h followed by calcination in the furnace at 400 °C, 600 °C, 700 °C, 800 °C and 1000 °C for 5 h with rate of 10 °C/min.

2.2. Catalytic testing

The catalytic reaction was performed in a fixed micro reactor coupled with Fourier Transform Infrared. The molar ratio reaction gas mixture of CO_2 and H_2 is 1:4 and was passed in heated isothermal tube furnace. A flow rate of $CO_2/H_2 = 50.00\ cm^3/min$ was used with the increment temperature rate of 5 °C/min.

2.3. Characterization

XRD analysis was conducted by using Diffractometer D5000 Siemens Crystalloflex with CuK_α radiation ($\lambda = 1.54060$ Å). The data obtained was analyzed by a PC interfaced to the diffractometer using software called Diffrac Plus. For FESEM analysis, sample was scanned using Zeiss Supra 35 VP FESEM operating of 15 kV. The catalyst sample was bombarded by electron gun with tungsten filament under 25 kV. N_2 adsorption-desorption isotherms for the catalysts were measured by Micromeritics ASAP 2010. The X-band Bruker electron spin resonance (ESR) spectrometer connected to a Thermo Scientific NESLAB chiller (ThermoFlex3500 model) to control water cooling temperature. The TPR-H_2 and TPD-CO_2 of the catalyst was carried out using Thermo Finnigan TPD/R/O 1100 fitted with a thermo conductivity detector (TCD) and controlled by a computer. The sample was placed in the quartz reactor and was heated from room temperature to 900 °C with heating rate 10 °C/min under a 30 mL/min of 5% H_2 in nitrogen for TPR and a flow of CO_2 (20 mL/min) for TPD analysis.

2.4. RSM for CO_2 methanation optimization over ru/mn/Ce(5:35:60)/Al_2O_3 catalyst

Optimization of Ru/Mn/Ce (5:35:60)/Al_2O_3 for methanation reaction was done using the Design-Expert 7.06 trial (Stat Ease, Inc. Minneapolis, USA). The studied parameters which are calcination temperature (600 °C–800 °C), ratio based loading (60%–80%), and catalyst dosage (3 g- 7 g) and the related parameter effects with response (CO_2 conversion) were analysed and optimized by Box-Behnken design. This parameter was selected based on experimental data obtained during catalytic screening. Fig. 1 showed the flowchart of response surface methodology using Box-Benhken design.

3. Results and discussion

3.1. Characterization

3.1.1. X-rays diffractogram analysis

The changes of phase obtained from XRD analysis for Ru/Mn/Ce (5:35:60)/Al_2O_3 catalyst upon the increase of calcination temperatures are shown in Fig. 2. It was observed that the crystallinity of the catalyst was amended as the calcination temperature increased. This result suggests that crystal lattice has been rearrangement in

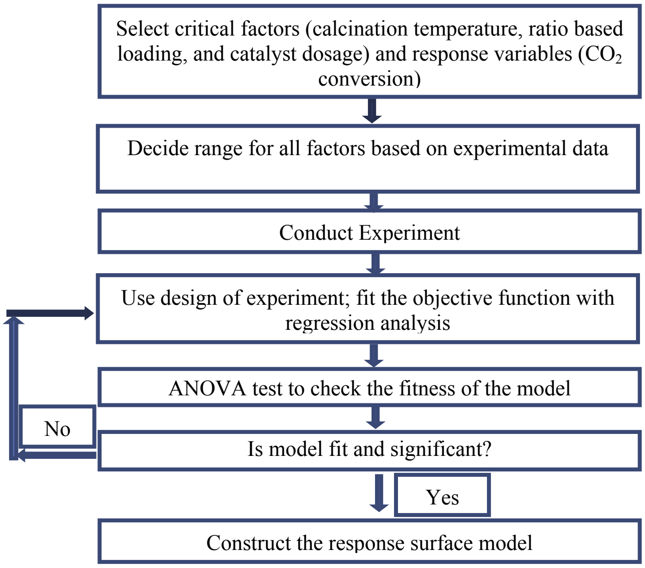

Fig. 1. Flowchart of response surface methodology.