Jurnal
Teknologi

Full Paper

OPTIMIZATION OF PRASEODYMIUM OXIDE BASED CATALYSTS FOR METHANATION REACTION OF SIMULATED NATURAL GAS USING BOX-BEHNKEN DESIGN

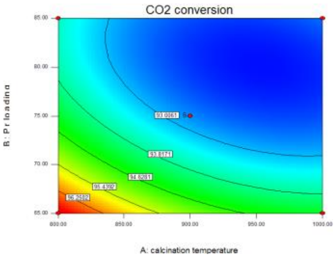
Salmiah Jamal Mat Rosid, Wan Azelee Wan Abu Bakar, Rusmidah Ali*

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

Article history
Received
16 February 2014
Received in revised form
20 January 2015
Accepted
15 June 2015

*Corresponding author
wazelee@kimia.fs.utm.my

Graphical abstract



Abstract

Malaysia energy demand on natural gas is increasing, leading to the purification of sour natural gas through the removal of carbon dioxide using catalytic conversion technique. Praseodymium oxide is preferred due to its properties which are suitable in the production of catalysers, polish glass and also as alloying agent. Therefore, a series of praseodymium oxide catalyst was prepared by incipient wetness impregnation method and was calcined at 400°C for 5 hours during screening reaction. The experimental Box-Behnken design was applied for optimizing the parameters in catalytic methanation reaction. The optimum parameters were found to be compatible with the experimental result which showed that Ru/Mn/Pr (5:35:60)/Al_2O_3 calcined at 800°C with 65% Pr loading and 7 g of catalyst dosage gave 96% of CO_2 conversion, determined using FTIR, and yielded about 41% of CH_4 at reaction temperature of 400°C. In the stability test, the catalyst's performance showed an increase and was stable up to 7 hours with 96% of CO_2 conversion. X-ray Diffraction (XRD) analysis showed an amorphous structure while Field Emission Scanning Electron Microscope (FESEM) illustrated the presence of small and dispersed particles with undefined shape covering the catalyst surface. EDX analysis revealed that when calcination temperature increased, the mass ratio of Ru increased. Meanwhile Nitrogen Adsorption (NA) analysis revealed that Ru/Mn/Pr (5:35:60)/Al_2O_3 catalyst attained surface area of 134.39 m^2/g.

Keywords: Natural gas, methanation reaction, praseodymium oxide, manganese oxide, ruthenium oxide, Box-Behnken design

Abstrak

Permintaan tenaga Malaysia pada gas asli semakin meningkat yang telah membawa kepada membersihkan gas asli masam dengan mengeluarkan karbon dioksida menggunakan teknik penukaran bermangkin. Praseodimium oksida dipilih kerana sifatnya yang sesuai untuk menghasilkan pemangkin, kaca menggilap dan juga sebagai ejen mengaloi. Oleh itu, satu siri oksida pemangkin praseodimium telah disediakan dengan kaedah kelembapan pengisitepuan dan telah dikalsin pada 400°C selama 5 jam pada reaksi pemeriksaan. Eksperimen Box- Behnken telah digunakan untuk mengoptimumkan parameter dalam tindakbalas metana pemangkin. Parameter optimum didapati serasi dengan keputusan eksperimen yang menunjukkan bahawa Ru/Mn/Pr (5:35:60)/Al_2O_3 dikalsin pada 800°C dengan 65% muatan Pr dan 7 g dos pemangkin memberikan 96% penukaran CO_2 yang ditentukan menggunakan FTIR dan menghasilkan kira-kira 41% CH_4 pada suhu 400°C. Ujian kestabilan menunjukkan bahawa prestasi pemangkin telah meningkat dan stabil sehingga 7 jam dengan 96% penukaran CO_2. X-ray Belauan (XRD) dan Padang Pelepasan Mikroskop Imbasan Elektron (FESEM) menunjukkan bahawa pemangkin adalah dalam struktur amorfus. Analisis EDX mendedahkan bahawa apabila suhu pengkalsinan meningkat, nisbah jisim Ru meningkat. Sementara itu analisis

Penjerapan Nitrogen mendedahkan bahawa Ru / Mn / Pr (5:35:60)/Al_2O_3 pemangkin mencapai luas permukaan 134.39 m^2/g.

Kata kunci: gas asli, metanasi, praseodimium oksida, mangan oksida, rutinium oksida, reka bentuk Box-Behnken.

1.0 INTRODUCTION

Natural gas is an extremely important source of energy for reducing pollution and maintaining a clean and healthy environment [1]. Gas Malaysia provides a clean, efficient, cost-effective and uninterrupted supply of natural gas or liquefied petroleum gas to industries, commercial businesses and homes. Even though Malaysia succeeds in the production of natural gas, it seems that the natural gas still consists more of the impurities that falls into sour gas and this will lead towards lower quality of Malaysia natural gas and price.

Due to stringent regulation on CO_2 content in commercial natural gas, high CO_2 content in natural gas must be removed. A variety of conventional separation methods are presently being used to remove the undesired gas fraction from crude natural gas. Although some of these processes have been proven successful for the selective removal of CO_2 from multi-component gaseous streams, they are still some drawbacks which are associated with large energy consumption, corrosion, foaminess and low capacity [2].

Methanation process has become a promising method which converts CO_2 to CH_4 by catalytic conversion reaction. Acidity of CO_2 requires the basicity of metal oxide to increase adsorption of acidic CO_2 on the catalyst surface. Rare earth weak basicity elements are known for their catalytic activity and were used as dopants in a variety of catalytic reaction [3]. In a previous research conducted by Fierro *et al.* (1985), praseodymium oxide based catalysts was used to study the dehydration and dehydrogenation reaction of 2-butanol [4].

Praseodymium oxide (Pr_6O_3) is the most active oxide among rare earth metals as it possesses multiple stable oxidation state [5]. A research conducted by Ferro (2011) indicated that the insertion of Pr_2O_3 in the Ni-S alloy increased the electro-catalytic activity for the 2-Butanol in 30% KOH solutions at room temperature due to the larger surface area and a more amorphous microstructure of the Ni-S when coated with Pr_2O_3 [6]. Therefore, in this research the role and performance of praseodymium oxide as based catalysts in catalytic methanation reaction was investigated. In addition, stability test was accomplished to investigate the robustness of the catalysts.

The important conditions used during catalyst activation (reduction) were also studied with the aim of improving catalyst performance by using response surface methodology (RSM). As reported by Toemen *et al.* (2014), the investigation of Ru/Mn/Ce/Al_2O_3 with three important parameters for CO_2 methanation were obtained in optimum value 10 g of catalyst dosage calcined at 1025°C with 65 wt% of Ce loading [7]. Therefore, the impact of three critical parameters (effect of calcination temperature, loadings of Pr and amount of catalyst dosage towards Ru/Mn/Pr/Al_2O_3) were studied.

2.0 EXPERIMENTAL

2.1 Preparation of Praseodymium Oxide by Incipient Wetness Method

A 5.00 g of praseodymium nitrate salts was dissolved with 5 mL of distilled water. Then the praseodymium solution was mixed with 0.98 g of manganese nitrate and 0.30 g of ruthenium chloride. Mixed catalysts solution was prepared by different ratio of base loading. The solution was then impregnated on Al_2O_3 bead supports for 15 minutes. It was then dried at 80°C for 24 hours and calcined at 400°C for 5 hours to convert the nitrate solution salts to oxides.

2.2 Catalytic Testing

The catalytic reaction was conducted under atmospheric pressure in a fixed micro reactor and analyzed via online Fourier Transform Infrared (Brand: Nicolet Avatar 370 DTGS Spectrophotometer). The reaction gas was passed through isothermal tube furnace in a molar ratio 1:4 of CO_2 and H_2, respectively. A flow rate of CO_2/H_2 = 50.00 cm^3/min was used with an increment temperature rate of 5°C/min.

2.3 Methane Formation

The Hewlett Packard 6890 Series Gas Chromatography System with capillary column (Brand: Ultra 1 932530) with 25.0 m × 200 μm × 0.11 μm nominal column was used in this research. Helium gas with the flow rate of 20 mL/min at the pressure of 75 kPa was used as carrier gas. The initial temperature was set at 50°C for 5 minutes and the injection temperature was 150°C. The detection temperature for this analysis was 310°C. The entire gas samples were then analyzed via Flame Ionization Detector (FID).

2.4 Response Surface Methodology

The levels of the significant parameters and the interaction effects with CO_2 conversion were analyzed and optimized using Box-Behnken design. In this study, 17 runs of experiment and the independent variables were studied at three different levels. Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA). This analysis included Fisher's F- test (overall model significance), it's associated probability p(F), correlation coefficient R, determination coefficient R^2 which measure the goodness of fit of regression model. For each variable, the quadratic models were represented as contour plots and response surface curves were generated using Design Expert software (Version 7.1.5, Stat-Ease Inc., Minneapolis, USA) statistical package.

2.5 Characterization

XRD analysis was performed using Cu Ka radiation (λ=1.54060 Å). Data were collected over a range of 2θ from 10° to 80° and analyzed by software called Diffract Plus. For EDX analysis, sample was scanned using Zeiss Supra 35 VP FESEM operating of 15 kV couple with EDX analyzer. The catalyst sample was bombarded by electron gun with tungsten filament under 25 kV resolutions. N_2 adsorption/desorption isotherm of the catalysts analysis 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.

3.0 RESULTS AND DISCUSSION

3.1 Characterization

Various characterization techniques have been applied to analyze the effect of CO_2/H_2 methanation reaction on the structural properties of the Ru/Mn/Pr (5:30:65)/Al_2O_3 catalyst calcined at different reaction temperatures. The fresh catalyst was referred to the catalyst before the methanation reaction.

X-Ray Diffraction (XRD)

The potential catalyst, which was Ru/Mn/Pr (5:30:65)/Al_2O_3 calcined at 800°C, 900°C and 1000°C, were analyzed by XRD in order to determine the active oxide phases which contribute to the good catalytic activity. The diffractograms of catalyst are shown in Figure 1

The differences in calcination temperature did not show any differences in XRD diffractogram as all the phases showed a low degree of crystallinity and broad peaks. Increase of the calcination temperature up to 1000°C resulted in the diffractogram showing slightly intense and narrower peaks, though they were not very significant due to the presence of praseodymium. Consequently, this indicated that the catalyst has small particle size with low degree of crystallite that contributes to the high catalytic activity. The peaks formed at 800°C were due to the presence of Al_2O_3 of cubic phase which were revealed at 2θ values of 67.110° (I_{100}), 37.511° (I_{69}), 45.600° (I_{65}), and 66.399° (I_{50}) $2\theta_{ref}$ values: 67.149°, 36.490°, 45.510°, and 66.351°) with d^*_{obs} values (Å) of 1.393, 2.395, 1.987 and 1.407 (d^*_{ref} values (Å): 1.393, 2.460, 1.991 and 1.407). On behalf of Ru/Mn/Pr (5:30:65)/Al_2O_3 catalyst calcined at 900°C and 1000°C, the peak of alumina cubic phase can be assigned at the same 2θ values of 800°C calcination temperature. Interestingly, the peak of RuO_2 can be observed at 2θ values of 28.089° (I_{100}), and 36.666° (I_{77}) $2\theta_{ref}$ values: 28.010°, 35.051°) with d^*_{obs} values (Å) of 3.174, and 2.448) (d^*_{ref} values (Å): 3.183, and 2.558). A new peak at 2θ values of 33.087° (I_{999}), 31.533 (I_{235}), and 46.888 (I_{235}) with $2\theta_{ref}$ values: 32.685°, 31.908°, and 46.389° with d^*_{obs} values (Å) of 2.702, 2.789, and 1.967 (d^*_{ref} values (Å): 2.737, 2.802, and 1.955) can be assigned as $PrMnO_3$.

FESEM Analysis

Figure 2 illustrates the morphology of Ru/Mn/Pr (5:30:65)/Al_2O_3 catalyst calcined at 800°C, 900°C, and 1000°C for 5 hours. The catalyst showed a rough and well dispersed surface with crystal shape. When the calcination temperature was increased to 900°C (Figure 2(b)), the pore of the catalyst was slightly visible and the clustered particle was well distributed. Interestingly, at 1000°C calcination temperature, the particles become connected to each other and were aggregated with undefined shape in a non-homogeneous distribution. Overall, the micrograph showed the non-uniformed surface which was believed to give easy access of adsorbed molecules to react. Moderate pore diameter and small particle size of the catalyst are important for high catalytic activity [8].

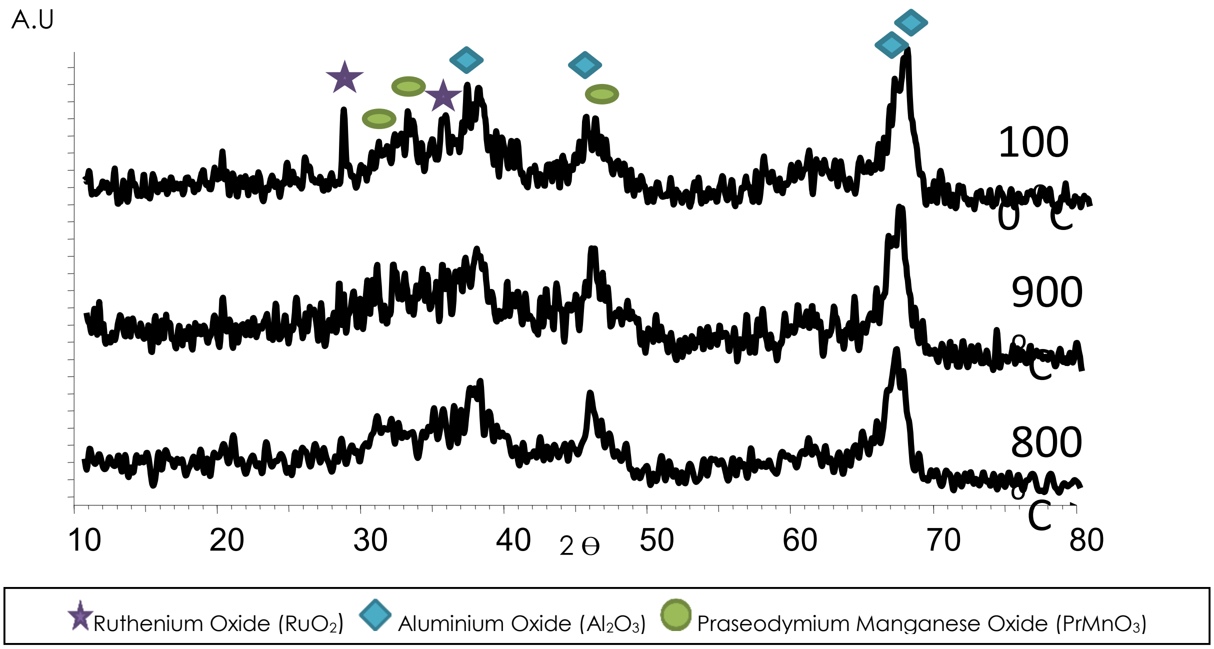


Figure 1 XRD Diffractograms of Ru/Mn/Pr (5:30:65)/Al_2O_3 catalysts calcined at (a) 800 °C, (b) 900 °C and (c) 1000 °C for 5 hours

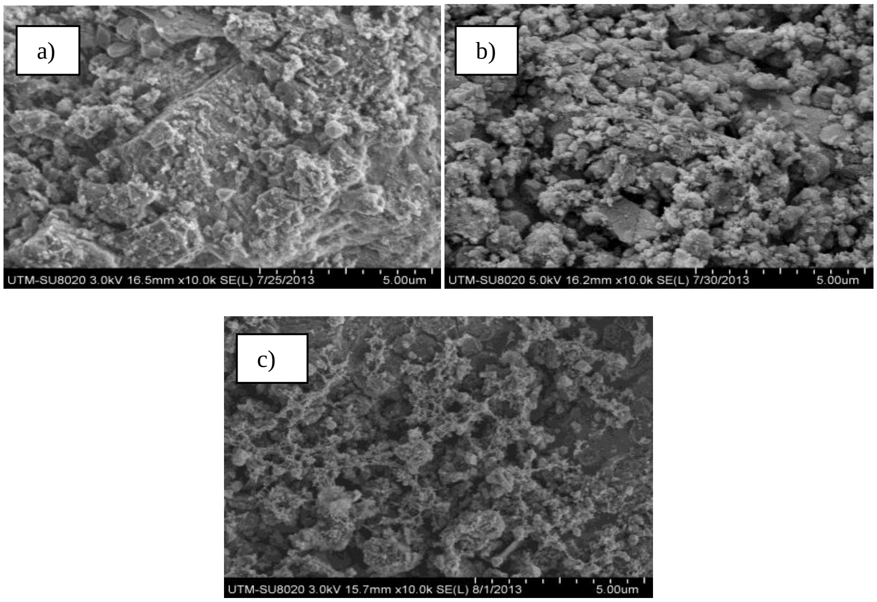


Figure 2 FESEM micrographs of Ru/Mn/Pr (5:30:65)/Al_2O_3 catalyst calcined at a) 800 °C b) 900 °C c) 1000 °C in 10000x magnification with scale bar: 500 nm

Energy Dispersive X-ray Analysis (EDX)

The composition of element present in the catalyst is summarized in the Table 1. From the table, the mass ratio of Ru was higher at 800°C and 1000°C; this was probably due to the migration of Ru into the catalyst surface. It can be also observed that the atomic ratio of Pr was higher compared to Mn and Ru for all different calcination temperatures. This was possibly due to the Pr that acted as a base in the catalyst. The mass ratio of Mn was lower on the catalyst surface due to high affinity of Mn to be absorbed into the pores of the alumina support.

BET Surface Area

BET surface area analysis in Table 2 shows that Ru/Mn/Pr (5:35:60)/Al_2O_3 catalyst attained surface area of 134.39 m^2/g. The surface area decreased as the calcination temperature was increased due to the aggregation of primary particles to secondary particles with formation of dense solid. The calcination temperature is 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 [9]. Although higher calcination temperature of Ru/Mn/Pr (5:35:60)/Al_2O_3 catalyst reduced the BET surface area, yet it has the benefit of securing the existence of stable structure on the catalyst. The isotherm showed a higher degree of mesopores that resembled the typical shape of Type IV isotherm, indicating more mesoporous characteristic. The monolayer adsorption was completed and the multilayer adsorption started to occur at low relative pressure. This was supported with the hysteresis loops at above 0.5 relative pressures. As relative pressure increased, the gas adsorption volume also increased, suggesting a capillary condensation phenomenon as mentioned by Liu *et al.* (2014) [10]. The initial uptake for 800°C was higher compared to 900°C and 1000°C due to presence of microspore structure in catalyst. This also caused the broader hysteresis loops which represented a lower degree of mesoporosity of the catalyst.

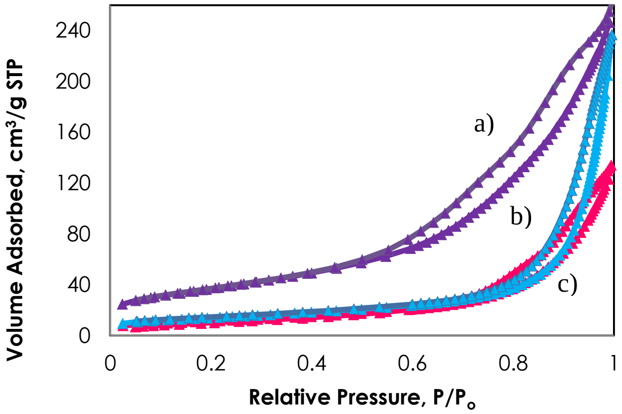


Figure 3 Isotherm plot of a) 800°C, b) 900°C, c) 1000°C of Ru/Mn/Pr(5:30:65)/Al_2O_3

3.2 Methanation Catalytic Screening Testing

A series of praseodymium oxide catalysts calcined at 400 °C were analyzed via online Fourier Transform Infrared for catalytic activity performance. All the prepared catalysts displayed a drastic increase of CO_2 conversion starting at reaction temperature of 200 °C. From Figure 4, both mono and bimetallic oxide catalysts showed low performance of CO_2 conversion. Therefore, the potential of Ru/Mn/Pr (5:30:65)/Al_2O_3 catalyst was optimized and screened for their catalytic activity.

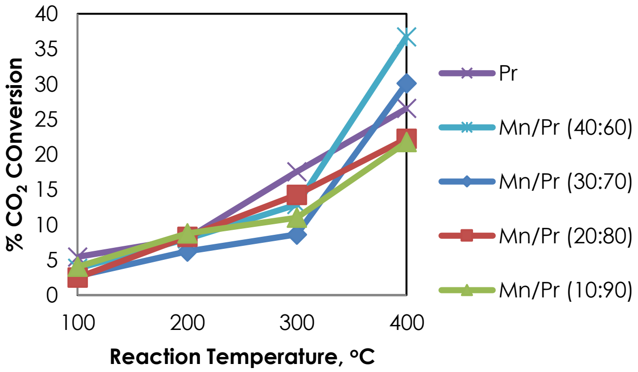


Figure 4 CO_2 conversions for catalytic screening of CO_2/H_2 methanation reaction over Pr/Al_2O_3 catalysts calcined at 400 °C

Table 1 Elemental composition from EDX analysis for Ru/Mn/Pr (5:30:65)/Al_2O_3 catalysts calcined at 800°C, 900°C, and 1000°C

Catalyst	Mass ratio (%)				
	Al	**O**	**Pr**	**Mn**	**Ru**
800	25.09	60.70	6.70	1.60	3.99
900	25.40	59.42	5.77	3.47	1.94
1000	24.45	61.98	6.67	0.87	3.91

Table 2 BET surface area and average pore diameter of the Ru/Mn/Pr (5:30:65)/Al_2O_3 catalyst calcined at 800 °C, 900 °C, and 1000 °C for 5 hours

Catalyst	Calcination temperature (°C)	Surface area (m^2/g)
Ru/Mn/Pr (5:30:65)/Al_2O_3	800	134.39
	900	130.62
	1000	87.65

3.2.1 Optimization of Catalyst

Calcination Temperatures

From the screening test of CO_2 conversion, it has been observed that Ru/Mn/Pr (5:30:65)/Al_2O_3 catalyst was the catalyst with the most potential among other studied catalysts. Further study on the potential catalyst with different calcination temperatures of 800°C, 900°C, and 1000°C for 5 hours was conducted. The result in Figure 5 reveals that the higher percentage conversion occurred at 350°C reaction temperature for 800°C, 900°C, and 1000°C calcination temperatures. This may have been due to the changes that occurred on the surface of the catalyst. It is in good agreement with Wan Abu Bakar *et al.* (2008) who claimed that several processes may occurred during calcination such as modification of structure and texture through the sintering process, active phase generation, loss of chemically bonded carbon dioxide or water and stabilization of chemical properties [11]. The high catalytic activity of catalysts was supported by XRD diffractogram which showed an amorphous phase and the presence of ternary species of $PrMnO_3$ at 1000°C that also caused a decrease in catalytic activity. FESEM micrographs showed a small particles size, indicating high surface area which was supported by BET analysis. EDX analysis revealed the excessive amount of Ru on the catalyst surface had decreased the catalytic activity.

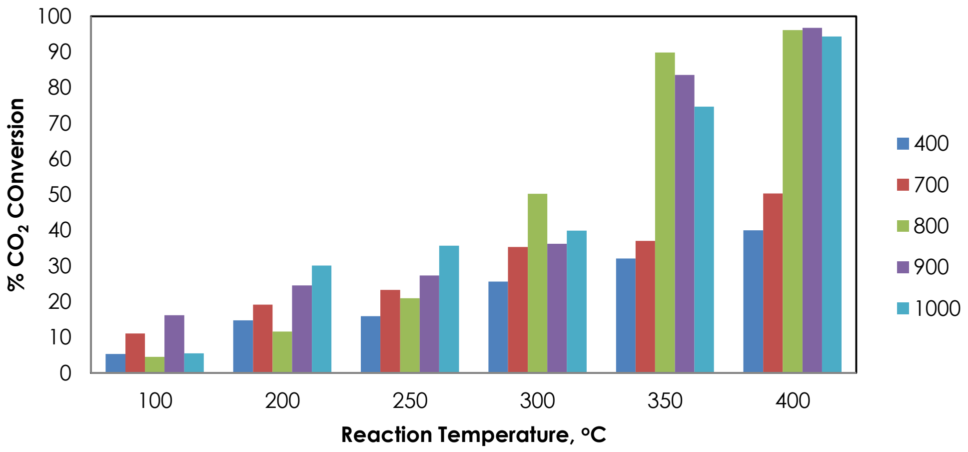


Figure 5 The trend plots of CO_2 conversion over Ru/Mn/Pr (5:30:65)/Al_2O_3 catalyst calcined at various temperatures, 400°C, 700°C, 800°C, 900°C and 1000°C for 5 h

Praseodymium Loadings

The effect of praseodymium loadings has been investigated and it showed that when the Pr content was increased, the CO_2 conversion decreased. It may have been due to blockage of active site by excessive loading of Pr. This is supported by He, *et al* (2011) who stated that the increasing Pr content provided a particle to nucleate, which inhibited the growth of crystal and followed by blocking the surface active site [12]. Therefore, the best ratio for Pr loading was 65 % which gave above 94 % of CO_2 conversion for each calcination temperature.

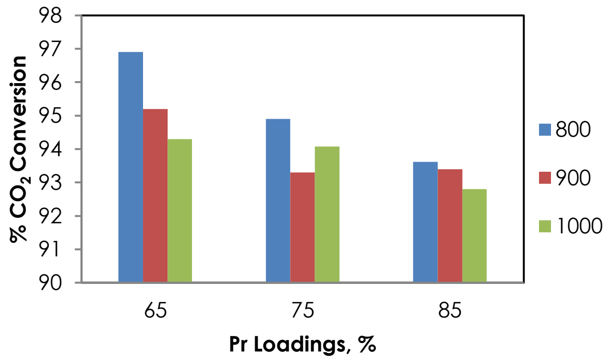


Figure 6 The trend plots of CO_2 conversion over Ru/Mn/Pr (5:30:65)/Al_2O_3 catalyst calcined at various calcination temperatures, 800°C, 900°C and 1000°C

Catalyst Dosage

Figure 7 shows that the increase of catalyst dosage caused a slight increase on the CO_2 conversion. This may be due to the increase of surface area on the catalyst that reacted with the flow of CO_2/H_2 gases during the reaction to convert CO_2 gas to CH_4 gas. Su, *et al* (2010) also stated that the efficiency of the degradation increased with the increase of the catalyst dosage [13].

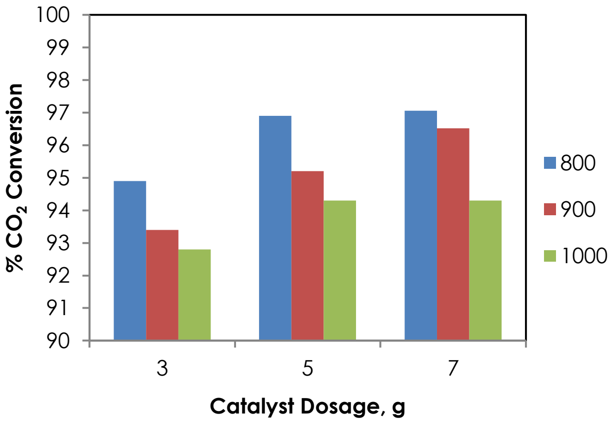


Figure 7 The trend plots of CO_2 conversion over Ru/Mn/Pr (5:30:65)/Al_2O_3 catalyst calcined at various catalyst dosages

3.2.2 Methane Formation

Figure 8 shows the comparison trend plot of CH_4 formation over the studied catalysts. The formation of methane over Ru/Mn/Pr (5:30:65)/ Al_2O_3 catalyst at 800°C was only 41 % at 400°C reaction temperature. Figure 8 also shows that at the initial temperature of 100°C and 200°C, no methane formation was produced. More formation of methane was expected at higher reaction temperature due to its highly exothermic reaction where methanation reaction is more favorable.

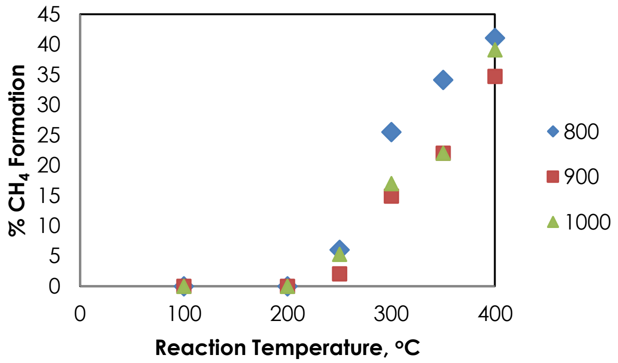


Figure 8 The methane formation over Ru/Mn/Pr (5:30:65)/Al_2O_3 catalyst calcined at 800 °C, 900 °C, and 1000 °C for 5 hours

3.3 Statistical Analysis

Table 3 lists the factors and levels for response surface method. The selection of levels was carried out on the basis of the results obtained in the preliminary study. The results obtained from the 17 experimental runs which were carried out according to the Box-Behnken design with three variables factor are summarized in Table 4.

Table 3 Levels of the optimization conditions

Factor	Independent Variables	Units	Low Level (-1)	High Level (+1)
A	Calcination Temperature	°C	800	1000
B	Praseodymium (Pr) Loadings	%	65	85
C	Catalyst Dosage	g	3	7

The evaluation of performance of the method showed that the model is significant and acceptable. The *p*-value of the model was smaller than 0.05 (p = 0.0000) and indicated a statistically significant relationship between the variables. The *p*-value of the lack-of-fit was higher than 0.05 (p = 0.8072) which was not significant and indicated that the proposed linear model fitted well for a significance level of 93 %. Table 5 also shows that parameters A, B, C, AB, and AC were significant as their *p*-value were lower than 0.05. In Table 6, the corresponding correlation coeffficient (R^2) was 0.9817 and indicated a large relationship between the variables. CV value (0.31 %) was smaller than 2.0 % and indicated a good precision.

Table 4 Experiment design for CO_2 conversion and results response

Run	**Calcination Temperature A (°C)**	**Pr Loadings B (%)**	**Catalyst Dosage C (g)**	**CO_2 Conversion (%)**	
				Actual	**Predicted**
1	1000	65	5	94.30	94.34
2	800	65	5	96.90	97.06
3	900	85	3	92.72	92.79
4	800	75	7	95.20	95.11
5	1000	75	3	92.13	92.22
6	900	85	7	93.40	93.53
7	900	75	5	93.30	92.79
8	900	75	5	92.80	92.79
9	900	75	5	92.40	92.79
10	1000	75	7	94.08	94.11
11	900	75	5	92.90	92.79
12	900	75	5	92.54	92.79
13	900	65	3	95.20	95.07
14	900	65	3	96.52	96.45
15	1000	85	5	92.80	92.64
16	800	85	5	93.62	93.58
17	800	75	3	94.90	94.87

Table 5 ANOVA table (partial sum of squares) for response surface model (response: CO_2 Conversion)

Source	**Sum of Squares**	**df**	**Mean Square**	**F value**	***p*-Value Prob>F**
Model	32.54	9	3.62	41.74	<0.0001 significant
A-Calcination Temp	6.68	1	6.68	77.11	<0.0001
B-Pr loading	13.47	1	13.47	155.48	<0.0001
C-Catalyst Dosage	2.26	1	2.26	26.07	0.0014
AB	0.79	1	0.79	9.14	0.0193
AC	0.68	1	0.68	7.86	0.0264
BC	0.10	1	0.10	1.18	0.3129
A^2	1.60	1	1.60	18.52	0.0036
B^2	4.21	1	4.21	48.58	0.0002
C^2	1.90	1	1.90	21.97	0.0022
Residual	0.61	7	0.087		
Lack of Fit	0.12	3	0.040	0.33	0.8072 not significant
Pure Error	0.49	4	0.12		
Cor Total	33.15	16			

In terms of coded factors, an empirical relationship has been expressed by the following quadratic Equation 1 where A is calcination temperature, B is Pr loading, and C is catalyst dosage:

$$CO_2 \text{ conversion} = +92.79 - 0.91A - 1.30B + 0.53C + 0.44AB + 0.41AC - 0.16BC + 0.62A^2 + 1.00B^2 + 0.67C^2 \qquad (1)$$

Table 6 Statistical information for ANOVA source response value

Std Dev	**0.29**	**R^2**	**0.9817**
Mean	93.87	Adj R^2	0.9582
CV %	0.31	Pred R^2	0.9194
PRESS	2.67	Adeq Precision	21.447

Figure 9 shows the predicted correlation and the actual values of CO_2 conversion. Figure 10-12 shows the contour plots of the predicted CO_2 conversion. The figures illustrate that the percentage of CO_2 conversion increases by increasing the calcination temperature, and catalyst dosage with lower Pr loadings. As can be seen in Figure 10-12, the CO_2 conversion increased remarkably with the increase of calcination temperature due to the fact that the calcination temperature has a significant impact on the catalytic activity. A higher Pr loading seemed to have caused a lowering of catalytic activity due to the excessive amount of Pr which could block the active site on alumina surface.

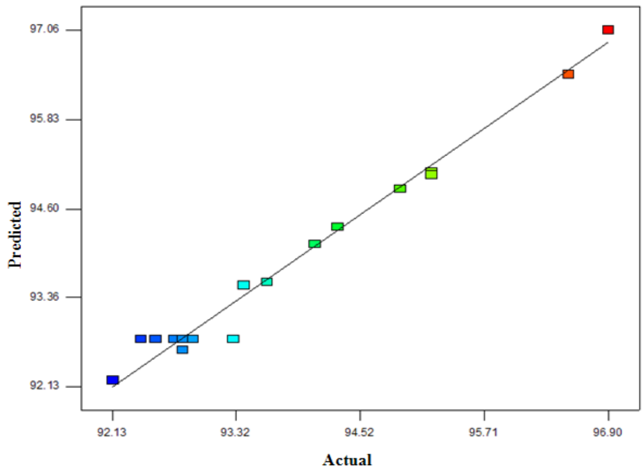


Figure 9 The predicted and actual values of CO_2 conversion

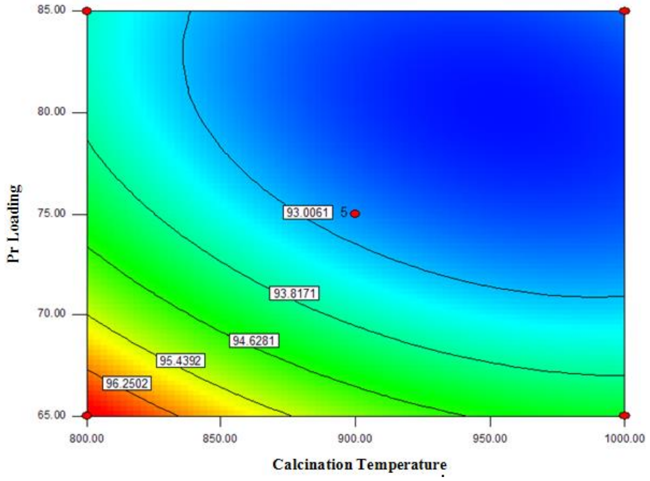


Figure 10 Contour plot of CO_2 conversion versus calcination temperature and Pr loadings. Fixed catalyst dosage (5 g)

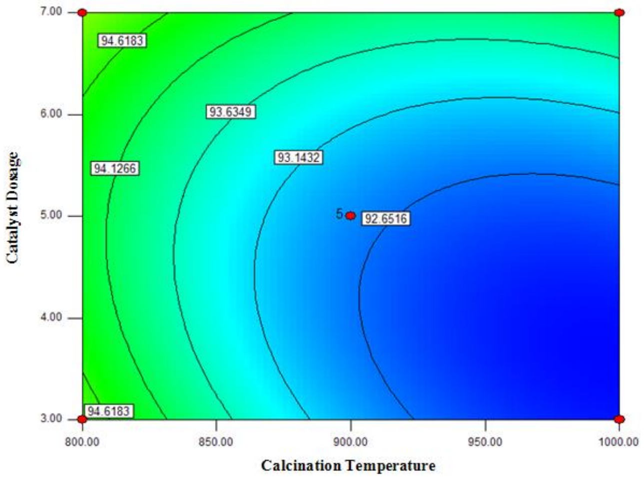


Figure 11 Contour plot of CO_2 conversion versus calcination temperature and catalyst dosage. Fixed Pr loading (75%)

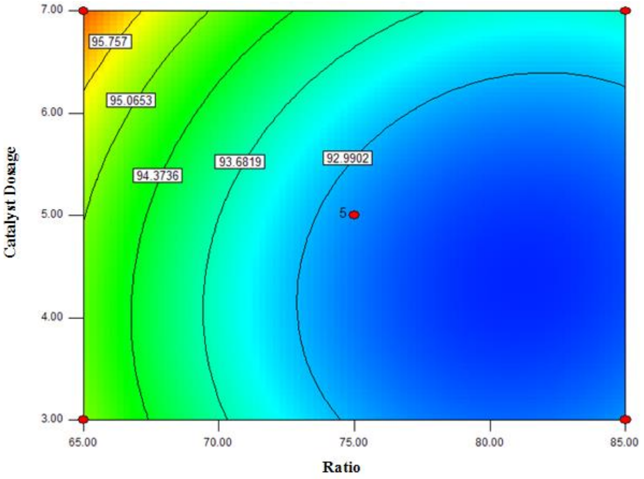


Figure 12 Contour plot of CO_2 conversion versus Pr loadings and catalyst dosage. Fixed calcination temperature (900°C)

3.3.1 Optimization

The goal of catalytic activity by Ru/Mn/Pr(5:30:65)/Al_2O_3 catalyst was to obtain optimum CO_2 conversion. For this purpose, the predictive model was determined using numerical hill-climbing algorithms. All the parameters were kept in range and the CO_2 conversion was set to 98% for the optimization. The best solution gave satisfying the above criteria are given calcination temperature of 800.17°C, Pr loadings 65.01%, and catalyst dosage 6.99 g and it has the overall desirability of 1.000. Contour plot given in Figure 13 shows the variation of CO_2 conversion with change in calcination temperature and Ru loadings when catalyst dosage was kept constant at optimum level of 6.97 g.

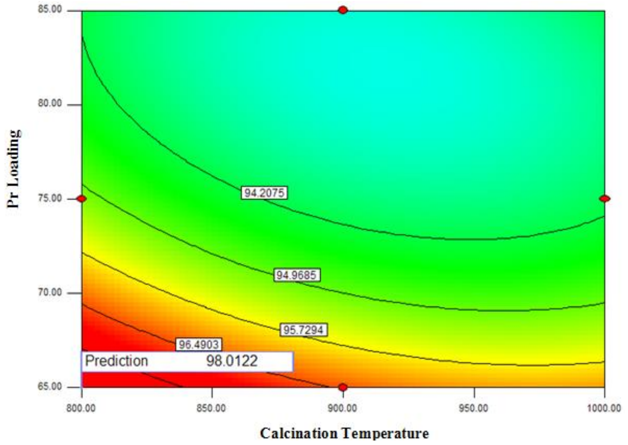


Figure 13 Contour plot of CO_2 conversion versus Pr loadings and calcination temperature

3.4 Stability Test of Catalyst

The catalytic stability of the potential Ru/Mn/Pr (5:30:65)/Al_2O_3 catalyst was investigated on stream for 7 h continuously at 400°C reaction temperature, as presented in Figure 14. The Ru/Mn/Pr (5:30:65)/Al_2O_3 catalyst showed good stability which was maintained unaffected for 7 h of maximum monitoring reaction time without deterioration. The CO_2 conversion of Ru/Mn/Pr (5:30:65)/Al_2O_3 catalyst was increased until 3 h and maintained at almost 98% throughout the reaction time. It showed that the addition of manganese and ruthenium may have assisted in maintaining the catalyst's stability during the reaction. This is in a good agreement with Zhao *et al*. (2012) who found that modifying the based with manganese significantly led to the most stable catalyst compared to the unmodified catalyst [14]. From these results, it can be concluded that the Ru/Mn/Pr (5:30:65)/Al_2O_3 catalyst was still active and stable even when it was left unattended for 7 h under 800°C calcination temperature.

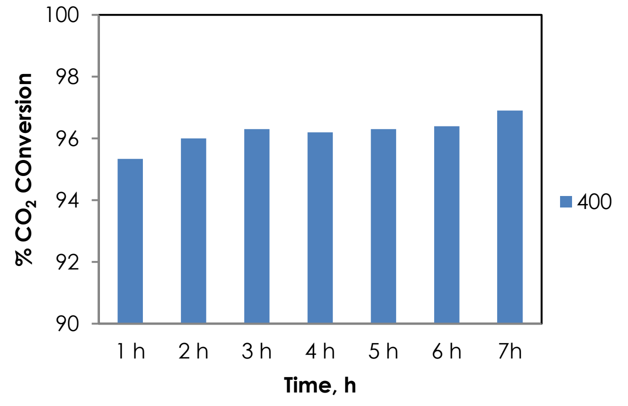


Figure 14 Stability test over Ru/Mn/Pr (5:30:65)/Al_2O_3 catalysts calcined at 800 °C with 400 °C reaction temperature

4.0 CONCLUSION

In this study, the Ru/Mn/Pr(5:30:65)/Al_2O_3 was assigned as a potential catalyst with percentage CO_2 conversion of 96% and 41% at 400°C reaction temperature. The suggested value from statistical model using Box-Behnken design very much agreed with the experimental value. XRD results showed that the presence of Pr in Ru/Mn/Pr (5:30:65)/Al_2O_3 catalyst would possess a low degree of crystallinity at calcination temperatures of 800°C, 900°C and 1000°C. FESEM images of Ru/Mn/Pr (5:30:65)/Al_2O_3 catalyst showed a rough surface morphology of the catalysts with a mixed of aggregation and agglomeration of particle. The elemental analysis performed by by EDX confirmed the presence of active species Mn, Ru, Pr, Al and O in the Ru/Mn/Pr (5:35:60)/Al_2O_3 catalyst and revealed the presence of $PrMnO_3$ species as inhibitor species which decreased the catalytic activity.

Acknowledgement

We are grateful to the Universiti Teknologi Malaysia, Ministry of Higher Education (MOHE), Malaysia for the financial support given under the GUP, Vot 04H97 and Ministry of Science, Technology and Innovation (MOSTI) for My Brain 15 (My PhD) scholarship to Salmiah Jamal Mat Rosid.

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