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OPTIMIZATION BY BOX-BEHNKEN DESIGN OF IN-SITU CARBON DIOXIDE CONVERSION USING LANTHANUM OXIDE

(Pengoptimuman Dengan Reka Bentuk Box-Behnken Untuk Penukaran In-Situ Karbon Dioksida Menggunakan Lantanum Oksida)

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Lanthanum oxide based catalyst was revealed as one of potential catalyst to convert carbon dioxide to wealth product methane in simulated natural gas. To produce higher conversion of carbon dioxide, the Response Surface Methodology utilizing Box-Behnken design (BBD) was used to optimize the lanthanum oxide based catalysts by three critical parameters which were calcination temperature, based ratio and catalyst dosage. The maximum CO_2 conversion was achieved at 1000 ^oC calcination temperature using 7 g of catalyst for 60% based loading. The optimization result from BBD is in good agreement with experimental data. The optimize parameters gave 99% of CO_2 conversion determined using Fourier Transformation Infrared (FTIR) and yielded about 50% of CH_4 at reaction temperature of 400 °C. X-ray Diffraction (XRD) analysis showed an amorphous structure with RuO_2 as active species and Field Emission Scanning Electron Microscope (FESEM) illustrated the catalyst surface was covered with small and dispersed particles with undefined shape. EDX analysis revealed that when the calcination temperature was increased, the mass ratio of Ru increased.

Keywords: Box-Behnken design, optimization, response surface methodology, lanthanum oxide

Abstrak

Mangkin asas lanthanum oksida adalah salah satu mangkin berpotensi menukarkan karbon dioksida kepada produk metana yang banyak dalam simulasi gas asli. Untuk menghasilkan penukaran karbon dioksida yang tinggi, kaedah gerak balas permukaan menggunakan reka bentuk Box-Behnken (BBD) untuk mengoptimumkan mangkin asas lantanum oksida oleh tiga parameter kritikal yang mana suhu kalsin, nisbah asas, dan dos mangkin. Maksimum penukaran CO_2 dicapai pada suhu kalsin 1000 ^oC menggunakan 7 g mangkin untuk 60% nisbah asas. Keputusan pengoptimuman dari BBD adalah selari dengan data eksperimen. Parameter yang optimum memberikan 99% penukaran CO_2 apabila ditentukan menggunakan Inframerah transformasi Fourier (FTIR) dan menghasilkan 50% metana pada suhu tindak balas 400 ^oC. Analisis pembelauan sinar-X (XRD) menunjukkan struktur amorfus dengan RuO_2 sebagai aktif spesis dan Mikroskop Imbasan Elektron Pancaran Medan (FESEM) menunjukkan permukaan mangkin diselaputi dengan partikel yang bersaiz kecik dan terserak sekata tanpa bentuk. Analisis EDX menunjukkan apabila suhu kalsin meningkat, nisbah jisim Ru meningkat.

Kata kunci: reka bentuk Box-Behnken, pengoptimuman, kaedah gerak balas permukaan, lantanum oksida

Introduction

Nowadays, industrial pollution control has facing challenges when industrial demands have been increased which would affect the environment and social sustainability. Therefore, new technologies are needed to reduce CO_2 emission at high efficiency to meet the requirement of Kyoto Protocol which has limited the greenhouse gas

emission to the environment. Natural gas is one of demanding industrial request for the fuel transportation. However, the higher percentage of CO_2 content in natural gas has been decreased the quality and price of natural gas.

Recently, the removal of these sour gases via chemical conversion techniques becomes the most promising technique. Catalysts for the CO_2 methanation have been extensively studied because of their application in the conversion of CO_2 gas to produce methane, which is the major component in natural gas [1]. Methanation of carbon dioxide is the reaction for chemical fixation of carbon dioxide that is considerably faster than the reactions to form other hydrocarbons or alcohols. Thus, the methanation reaction is suited for treating a huge amount of carbon dioxide [2]. Besides, methanation has received attention from a viewpoint of environmental protection because the emission of CO_2 in the atmosphere brings about global warming by the greenhouse effect and these harmful gases can simultaneously be converted to useful methane gas [3]. This process can increase the purity and quality of the natural gas without wasting the undesired components but fully used them to produce high concentration of methane.

From the previous study, trimetallic Ru/Co/La (5:35:60)/Al_2O_3 calcined at 1000 ^oC showed a promising performance with 99% of CO_2 conversion and 50% CH_4 formation [4]. This observation showed that La_2O_3 is able to increase adsorption of CO_2 to the surface of catalyst. Other than that, Wan Abu Bakar et al. also reported that when cobalt oxide doped with noble metal (platinum), it gives higher CO_2 conversion with 70% and yielded 47% methane [5]. This can be concluded that noble metal would increase the cobalt reducibility in catalyst supported on alumina [6]. Therefore, in this paper, the potential catalyst was optimized to determine the optimum parameters for Ru/Co/La (5:35:60)/Al_2O_3 to obtain higher CO_2 conversion and CH_4 formation by using Box-Behnken design.

Materials and Methods

Catalyst preparation

Wet impregnation method was used to prepare Al_2O_3 supported catalyst by impregnating the catalyst solution on Al_2O_3 beads support. Then, alumina beads with diameter of 3 mm was immersed into the catalysts solution for 20 minutes and it was then dried at 80 ^oC for 24 hours and calcined at 400 ^oC, 700 ^oC, 900 ^oC, 1000 ^oC, and 1100 ^oC for 5 hours. For catalytic activity measurements, reactions of methanation were performed from ambient temperature up to 400 ^oC with temperature rate of 5 ^oC/ min. CO_2 and H_2 gases were introduced into the reactor system in a stoichiometric ratio of 1:4. Screening on the product gas stream was done by using FTIR analysis.

Characterization

The surface morphology and physical properties of the catalysts were characterized by Field Emission Scanning Electron Microscope (FESEM) – Energy Dispersion X-ray (EDX), and X-ray Diffraction (XRD). The surface morphology of the samples was analyzed using Zeiss Supra 35VP FESEM with the energy of 2.0 kV and 50 000 x magnification couple with EDX analyzer and 1500x magnification. Prior to the analysis, the sprinkled sample was coated with gold as conducting material by gold sputter at 10^{-1} Mbar using Bio Rad Polaron Division SEM coating system machine. The XRD patterns of the powder samples were recorded at 2θ between 10^o to 80^o using a Bruker Advance D8 with Siemens 5000 diffractometer. The Cu K_α radiation operates at 40 kV and 40 mA with $\lambda = 1.5418$ Å.

Design of experiment

A three variables Box-Behnken design for response surface methodology were used to study the effect of calcination temperature (^oC), Based loadings (%), and catalyst dosage (g) on catalytic activity of methanation reaction using Design Expert Software, version 7.1 (Stat-Ease Inc., USA). Analysis of variance, ANOVA, is a statistical decision-making tool used for detecting any differences in average performances of tested parameters [7]. Analysis of variance (ANOVA) was used to check the adequacy of the model for the responses in the experimentation.

Results and Discussion

Characterization: X-ray diffractogram analysis for lanthanum oxide based catalyst

Figure 1 shows the diffractogram of Ru/Co/La (5:35:60)/Al_2O_3 calcined at 400 °C, 700 °C, 900 °C, 1000 °C and 1100 °C. XRD diffractogram for calcination temperature of 400 ºC showed very low degree of crystallinity and an amorphous phase. This could be attributed to the alumina support which can be assigned at 2θ of 66.47 ° (I_{100}) as Al_2O_3 with cubic phase. Tang et al. claimed that the support only exhibits broad diffraction peaks when calcined at below 500 ºC [8].

For Ru/Co/La (5:35:60)/Al_2O_3 calcined at 700 °C, the diffractogram also showed an amorphous peak indicating the atom are arranged almost in a regular pattern. At calcination temperature of 700 °C, three peaks of Al_2O_3 with cubic phase were appeared at 2θ = 45.83 ° (I_{100}), 66.97 ° (I_{100}), and 60.45 ° (I_{75}). Furthermore, at 900 °C calcination temperature exhibited of Al_2O_3 cubic phase which could be observed at 2θ values of 67.034º (I_{100}), 45.863º (I_{100}), and 37.604º (I_{80}). The shifting peaks occurred due to decrease lattice spacing parameter which can be supported by decreasing lattice value from 0.991 Á (110) to 0.246 Á (440) [9]. The peaks for cobalt oxide were only observed at 32.173º (I_{662}). Formation of new peak which belong to RuO_2 with tetragonal phase were revealed at the 2θ values of 28.135º (I_{999}), and 35.793º (I_{751}).The diffractograms of catalyst calcined at 1000 °C and 1100 °C exhibited similar peaks with the catalyst calcined at 900 °C. Nevertheless, the diffractogram of catalyst calcined at 1100 °C showed few new peaks. Three of them were at 2θ values of 33.958º, 36.146º, and 42.741º which were assigned to the lanthanum aluminium oxide with hexagonal phase. Other peaks corresponding to the alumina corundum with rhombohedral phase could be observed at 2θ values 43.347º and 57.492º. From the overall diffractograms, it could be suggested that the calcination temperature affects the performance of catalytic activity by increasing of crystal lattice in order to produce narrower peaks [10].

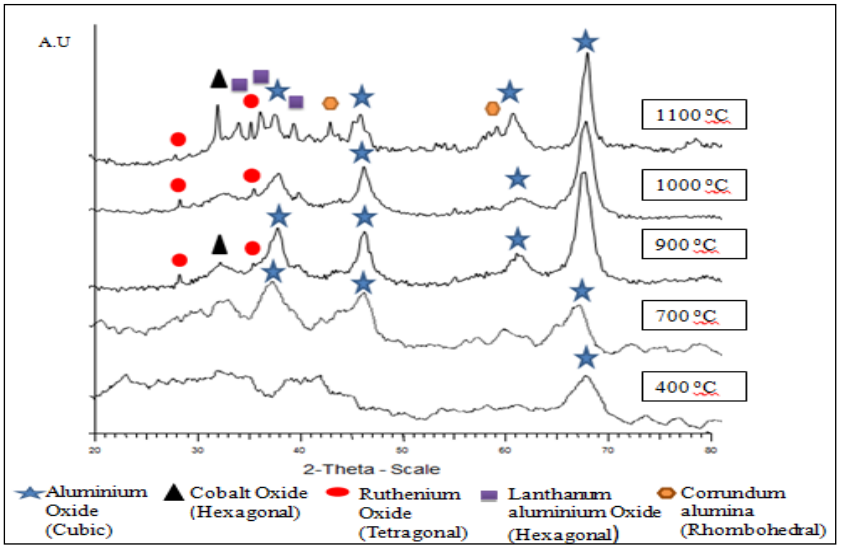

Figure 1. Diffractogram of various calcination temperatures of Ru/Co/La (5:35:60)/Al_2O_3 catalysts

Field emission scanning electron microscope analysis for lanthanum oxide based catalyst

The micrographs of the supported catalysts showed a rough surface morphology. In general, there was no significant change in morphologies for the entire sample after calcination. A typical FESEM micrograph for Ru/Co/La (5:35:60)/Al_2O_3 sample is illustrated in Figure 2. From the micrograph in Figure 2, the surface particles of the fresh catalyst agglomerated, possibly due to the calcination process. The particles were in spherical shape. It was also noted that the pore of the catalyst is slightly visible. When it is small particle, the surface area is higher thus, adsorption process easy to occur. This is in a good agreement with the XRD analysis which exhibited very broad peaks denoting an amorphous character for the Ru/Co/La (5:35:60)/Al_2O_3 catalyst. Nevertheless, the catalyst Ru/Co/La (5:35:60) /Al_2O_3 calcined at 1100 °C showed many square shaped particles were formed on

the catalyst surface. This square shaped was belong to Al_2O_3 rhombohedral phase as shown in the XRD diffractogram in Figure 1 as similarly discussed by Mat Rosid et al. [4].

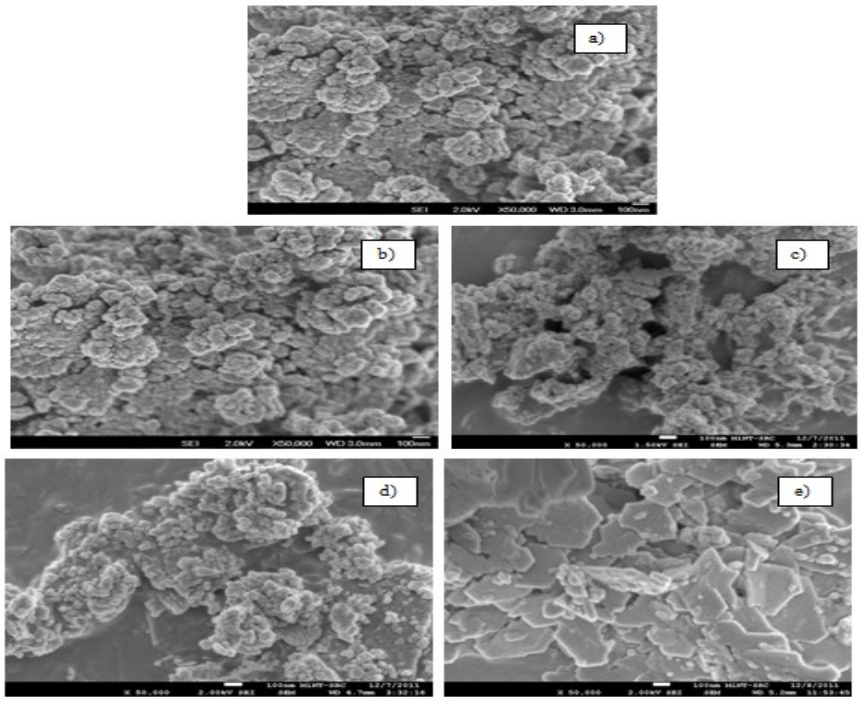

Figure 2. FESEM micrographs of Ru/Co/La (5:35:60)/Al_2O_3 catalyst calcined at a) 400 ^oC, b) 700 ^oC, c) 900 ^oC, d) 1000 ^oC and e) 1100^oC for 5 hour in 50000x magnification

Energy dispersive X-ray analysis for lanthanum oxide based catalyst

Table 1 shows the elemental composition of the EDX analysis for Ru/Co/La (5:35:60)/Al_2O_3 catalyst calcined at 400 ^oC, 700 ^oC, 900 ^oC, 1000 ^oC and 1100 ^oC. From the table, it was observed that atomic ratio of Al is quite high which suggested that the catalyst surface is dominated by the Al from the support. The entire elements were detected on the catalyst surface. At 1000 ^oC calcination temperature, the La and Co revealed the higher atomic ratio compared to Ru. It might due to Ru have been incorporated into the pore of alumina. Although the tiny amount of atomic mass of Ru on the catalyst surface, it still enhances the high catalytic activity towards methanation reaction [11].

Table 1. Elemental composition from EDX analysis at various calcination temperatures for 5 hours

Calcination Temperature (^oC)	**Atomic Ratio (%)**				
	Al	**O**	**La**	**Co**	**Ru**
400	35.72	44.14	4.58	1.69	0.13
700	36.48	42.68	3.16	1.81	0.35
900	36.89	52.47	5.94	1.89	0.40
1000	32.83	20.73	11.45	7.38	0.42
1100	43.96	40.28	8.57	5.56	0.47

Catalytic activity measurement: Effect of calcination temperature

From the catalytic screening of CO_2 conversion, the potential catalysts which was Ru/Co/La/Al_2O_3 catalyst was proceed with different calcination temperatures to elucidate the optimum calcination temperature on the potential catalyst. The catalytic activity is summarized in Table 2. The Ru/Co/La/Al_2O_3 catalyst showed an increasing catalytic activity with Co as a dopant with increasing calcination temperature. It was possibly due to the Ru enhance the dispersion of Co on the catalyst surface. It also has been reported by Kok et al. that La^{3+} promotes for the formation of new active sites while Ru could increase the degree of Co reduction and this improve the catalytic activity [12]. According to Perego and Villa, calcination process would give some effects towards the catalyst such as loss of chemically bonded water or CO, modified the texture and structure through sintering, generate active phase and stabilize the mechanical properties [13].

Table 2. Percentage conversion of CO_2 in CO_2/H_2 methanation reaction catalyzed by lanthanum oxide based catalysts with dopant (Co) and co-dopant (Ru) after calcined at different temperatures for 5 hours

Catalyst	Calcination Temperature (°C)	Reaction Temperature (°C)					
		100	200	250	300	350	400
		% Conversion of CO_2					
Ru/Co/La (5:35:60)/Al_2O_3	400	2.18	14.69	25.62	29.45	30.79	32.89
	700	4.30	33.04	66.93	70.09	74.83	89.09
	900	3.93	18.73	59.34	73.21	82.11	91.03
	1000	9.98	35.23	54.76	68.41	78.67	98.87
	1100	10.36	38.04	60.74	73.98	87.41	94.22

Effect of based loadings

The plot effect of based loadings is shown in Figure 3. The results obtained showed that when the based loading of La was increased, the CO_2 conversion was decreased. This might due to excessive amount of La has been blocking the active surface on catalyst. This re supported with He et al. 2011 [14] and Mat Rosid et al. 2015 [15] which have stated that excessive amount of based loading will enhance the particle to nucleate which will inhibit the growth of crystal on active site. Therefore, the optimum based loading was obtained at 60%.

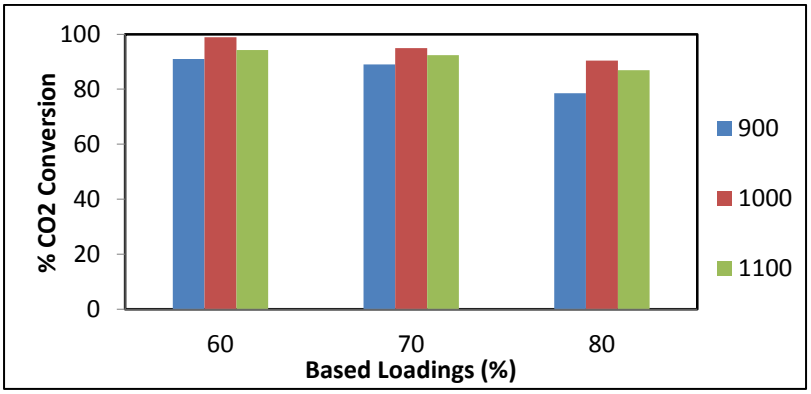

Figure 3. Catalytic performance of CO_2 conversion from methanation reaction over Ru/Co/La/Al_2O_3 catalyst calcined at 900 °C, 1000 °C and 1100 °C for 5 hours with various based loadings

Effect of catalyst dosage

Catalyst dosage is one of the parameter that affects the catalytic activity. Figure 4 shows that when the catalyst dosage is increase, the CO_2 conversion is increased. This is in agreement with Londhe and Gupta study which stated that when the catalyst dosage is increased, the fraction of the gases adsorbed over catalyst surface and the reaction products formed is increased [16].

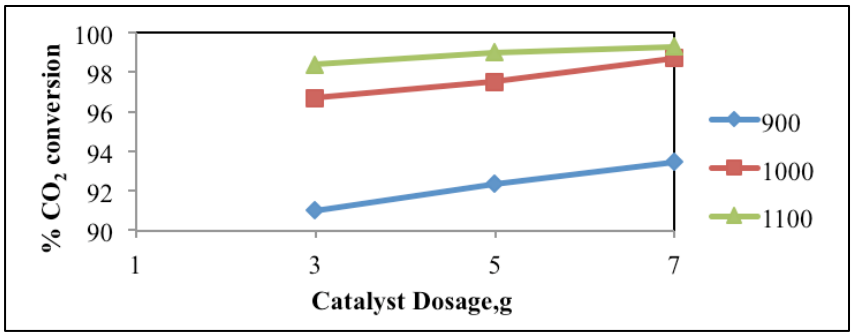

Figure 4. Catalytic performance of CO_2 conversion from methanation reaction over $Ru/Co/La/Al_2O_3$ catalyst calcined at 900 ^oC , 1000 ^oC and 1100 ^oC for 5 hours with various catalyst dosages

Methane gas formation

The formation of methane over the potential catalyst showed low percentage of methane at lower temperature which yielded 2.74% and 8.51% at 200 ^oC and 250 ^oC, respectively. However, when the reaction temperature reached 300 ^oC, the percentage formation of methane yielded 43.40% of CH_4. The increased of methane formation was 50% at 400 ^oC reaction temperature as discussed by Mat Rosid et al. [4].

Statistical analysis: Box-Behnken design

The selection of levels was carried out based on the results obtained in the preliminary study. Table 3 shows the experiment design for CO_2 conversion with 17 runs of experiment. The predicted values are accordance with actual value from the experimental data. Results obtained after carrying out ANOVA is presented in Table 4. The Model F-value of 122.87 implies the model was significant. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, A^2, B^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. From the ANOVA, it can be observed that catalyst dosage (c) is not a significant model terms. This can be supported from the experimental data which showed that the CO_2 conversion (Figure 4) does not highly differ for each catalyst dosage. The "Lack of Fit F-value" of 0.28 implies the Lack of Fit is not significant relative to the pure error. Non-significant lack of fit is good.

Table 3. Experiment design for CO_2 conversion and results response

Run	Calcination Temperature A (^oC)	Based Loadings B (%)	Catalyst Dosage C (g)	CO_2 Conversion (%)	
				Actual	Predicted
1	900	70	3	90.80	90.85
2	1000	60	7	98.87	98.79
3	1000	70	5	93.45	93.46
4	900	70	7	93.30	93.42
5	1100	80	5	90.30	90.38
6	1000	70	5	93.84	93.46
7	1000	80	7	93.00	92.97

Table 3 (cont'd). Experiment design for CO_2 conversion and results response

Run	Calcination Temperature A (^oC)	Based Loadings B (%)	Catalyst Dosage C (g)	CO_2 Conversion (%)	
				Actual	Predicted
8	1000	80	3	94.56	94.64
9	900	60	5	92.00	91.92
10	1000	70	5	93.00	93.46
11	1100	70	7	93.50	93.45
12	1000	70	5	93.80	93.46
13	1000	60	3	97.80	97.83
14	1000	70	5	93.80	93.46
15	1100	70	3	94.40	94.24
16	900	80	5	90.50	90.37
17	1100	60	5	97.70	97.83

Table 4. 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	102.99	9	11.44	122.87	<0.00001 Significant
A-Calcination Temp	17.46	1	17.46	187.51	<0.00001
B-Ratio	40.55	1	40.55	435.33	<0.00001
C-Catalyst Dosage	0.25	1	0.25	2.67	0.1464
AB	8.70	1	8.70	93.44	<0.0001
AC	0.19	1	0.19	2.08	0.1926
BC	1.73	1	1.73	18.57	0.0035
A^2	21.51	1	21.51	230.96	<0.0001
B^2	8.58	1	8.58	92.09	<0.0001
C^2	5.79	1	5.79	62.12	0.0001
Residual	0.65	7	0.093		
Lack of Fit	0.11	3	0.038	0.28	0.8390 not significant
Pure Error	0.54	5	0.13		
Cor Total	103.64	16			
Std. Dev	0.31		R^2	0.9937	
Mean	93.62		Adj R^2	0.9856	
CV	0.33		Pred R^2	0.9745	
PRESS	2.65		Adeq Precision	35.968	

To modify regression model accuracy, the ultimate model equation in terms of coded factors after excluding the insignificant items was obtained as follows:

$$CO_2 \text{ conversion} = 93.46 + 1.48A - 2.25B - 0.18C - 1.47AB - 0.22AC - 0.66BC - 2.26A^2 + 1.43B^2 + 1.17C^2$$

Optimization of parameters by Box-Behnken design

The optimization of critical parameters was run to obtain highest CO_2 conversion by using numerical hill-climbing algorithms. The CO_2 conversion was set to 99% and all parameters was kept in range. The optimum parameters were verified experimentally and it give almost exact value of CO_2 conversion as suggested by Box-Behnken design.

Conclusion

The Box-Behnken design was successfully applied for the optimization of catalytic methanation reaction to give the optimum parameters to obtain highest CO_2 conversion. The maximum CO_2 conversion was achieved at 1000 ^oC calcination temperature using 7 g of catalyst for 60% based loading. The optimize parameters gave 99% of CO_2 conversion determined using FTIR and yielded about 50% of CH_4 at reaction temperature of 400 °C. The active species in this methanation reaction was RuO_2 as observed in X-ray Diffraction (XRD) analysis and Field Emission Scanning Electron Microscope (FESEM) illustrated the catalyst surface was covered with small and dispersed particles with undefined shape. EDX analysis revealed that when calcination temperature increased, the mass ratio of Ru increased.

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