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Bulletin of Chemical Reaction Engineering & Catalysis, 14 (3) 2019, 678-682

Research Article

Basicity Optimization of KF/Ca-MgO Catalyst using Impregnation Method

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Received: 25th January 2019; Revised: 11th May 2019; Accepted: 20th May 2019; Available online: 30th September 2019; Published regularly: December 2019

Abstract

This research aimed at determining the optimum value between calcination temperature (X_1), calcination time (X_2) and %wt KF (X_3) toward optimum basicity of KF/Ca-MgO catalyst. Approximately 2-4%wt KF was added to the KF/Ca-MgO catalyst using the impregnation method to assist the Ca-MgO, at 450-550 °C and a calcination time of 2-4 hours. Furthermore, its basicity was analyzed using Tanabe's titration method. The use of Variance Analysis (ANOVA), indicated that calcination temperature (X_1) factor achieved the highest basicity of KF/Ca-MgO catalyst, as indicated by its high *F*-value (16.46262) and low *p*-value (0.0067). The correlation between each operating variables and the responses were shown in a mathematical equation. The optimization value is estimated by limiting the calcination temperature from 415.9 to 584.1 °C, with a calcination time ranging from 1.32 to 4.68 hours, and %wt KF of 1.3182 to 4.6818 % that obtained 1.18 mmol/g for the optimal catalyst basicity.

Keywords: KF/Ca-MgO catalyst; Basicity; Optimization; Response Surface Methodology

How to Cite: Anggoro, D.D., Buchori, L., Sasongko, S.B., Oktavianty, H. (2019). Basicity Optimization of KF/Ca-MgO Catalyst using Impregnation Method. *Bulletin of Chemical Reaction Engineering & Catalysis*, 14(3): 678-682 (doi:10.9767/bcrec.14.3.4248.678-682)

Permalink/DOI: https://doi.org/10.9767/bcrec.14.3.4248.678-682

1. Introduction

Potassium Fluoride (KF) is an alkaline halide molecule with an active and reactive F (fluorine) element, making it easier to rebound with metals. An increase in its effects leads to a higher catalyst activity [1-5]. However, when it is added in surplus, it decreases the catalyst activity. This has been proven by Wen *et al.* [6] during research by adding KF in CaO, where its addition above 25%, decreased the catalyst activity. When the amount is large, it covers the surface of the catalyst, thereby reducing its activity. Hu *et al.* [7] also conducted a study of the addition of KF in several catalysts, such as $CaO-Fe_3O_4$, $SrO-Fe_3O_4$, and $MgO-Fe_3O_4$ in which each had the optimum condition with the addition of KF. This was shown from the acquisition of biodiesel. According to Hu *et al.* [7], the obtained biodiesel was high assuming the addition of KF reaches 25% for CaO, 35% for MgO, and 10% for SrO.

The dispersion of active metals to the surface of the solid material is capable of expanding the catalyst surface and increasing the number of

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active sites. Furthermore, when the contact between the reactants and the catalyst increases, the reaction would be more comfortable and faster [8-13]. Another aim of using the carrier is to regulate the amount of metal required as well as to increase the catalyst activity and workability [14-15].

The classical method of optimization involves varying one parameter at a specific time while keeping the other constant. However, this method is inefficient as it fails to understand the relationships between variables (reaction time, temperature, molar ratio) and percentage yield [16-17]. Response Surface Methodology (RSM) is a valid statistical technique used to estimate complex processes. Its main advantage is in the reduction of experimental runs number required to provide adequate acceptable information statistically. It is an easy and cheap technique used to gather research results than the classical method [18]. RSM technique has been successfully applied in the field of quality experimental work [19-22].

The treatment processes/sol-gel used in this research is in three stages, namely impregnation, drying, and calcination. Furthermore, the study aims to analyze the optimum basicity of KF/Ca-MgO catalyst (Y) concerning calcination temperature (X_1), calcination time (X_2), and %wt KF (X_3).

2. Materials and Methods

Magnesium acetate, calcium nitrate, and citric acid compounds were weighed according to the predetermined calculations and dissolved in 95% ethanol. All three solutions are stirred at 350 rpm with the temperature of sol at 80 ºC until the color became clear. The formed gel was then dried at 110 °C for 6 hours by using an oven. The catalyst obtained was mashed using a mortar and calcined for 3 hours at 550 °C using a furnace. Impregnation of Ca-MgO will be achieved by dissolving KF with %wt between the ranges of 2-4 % in deionized water, after which it was stirred for 1 hour. Furthermore, the absorbed water was extracted from the catalysts surface by exposing it to 140 ºC for 6 hours and calcined at 450-550 ºC with a time range of 2-4 hours. The basicity of KF/Ca-MgO catalyst was further analyzed using the Tanabe's titration method.

3. Results and Discussion

The experimental design matrix designed using the central composite design method and results of the basicity of KF/Ca-MgO catalyst values are shown in Table 1. The result consists of 16 sets of coded condition expressed in natural values. The design consists of eight factorial, six axial, and three central points. The sequence of the experiment was randomized to minimize the effects of uncontrolled factors.

The Analysis of Variance (ANOVA), used to analyze the basicity of KF/Ca-MgO catalyst was shown in Table 2. The significance between each factor stated in Table 2 was tested

Table 2. Basicity value of catalyst at various %wt KF, calcination temperature, and calcination time

Run	Calcination Temperature (X_1, ºC)	Calcination Time (X_2, minutes)	%wt KF (X_3, %)	Basicity (mmol/g)
1	450	120	2	0.30
2	450	120	4	0.64
3	450	240	2	0.54
4	450	240	4	1.04
5	550	120	2	0.84
6	550	120	4	0.98
7	550	240	2	0.66
8	550	240	4	1.18
9	416	180	3	0.28
10	584	180	3	0.72
11	500	79	3	0.92
12	500	280	3	1.16
13	500	180	1.32	0.96
14	500	180	4.68	1.10
15(C)	500	180	3	1.06
16(C)	500	180	3	1.04

Table 1. ANOVA results (df: degree of freedom)

Variant	Coefficient	F-*value*	df	*p-value*
X_0 (const.)	1.056990			
X_1	0.137659	16.46213	1	0.006670
X_1^2	-0.211329	26.31767	1	0.002157
X_2	0.077883	5.26935	1	0.061478
X_2^2	-0.020410	0.24547	1	0.637901
X_3	0.127075	14.02814	1	0.009561
X_3^2	-0.023945	0.33789	1	0.582214
$X_1 X_2$	-0.077500	3.05647	1	0.131003
$X_1 X_3$	-0.022500	0.24762	1	0.629872
$X_2 X_3$	0.067500	2.31859	1	0.178664

using the *F*- and *p*- values. High *F* and *p* values lower than 0.05 indicates that the variables significantly influenced the response studied. The *F*-value illustrates the ratio between Mean Square of Factor (MSF) and Mean Square of Error (MSE). The effect of operating these variables is shown in Table 2.

The higher basicity of high *F*-value (16.462) and low *p*-value (0.0067) was illustrated in ANOVA Table 2. The objective function of this test is used to determine the optimum basicity value between calcination temperature, time, and %wt KF. The relation between each operating variables and the responses is shown in Equation (1).

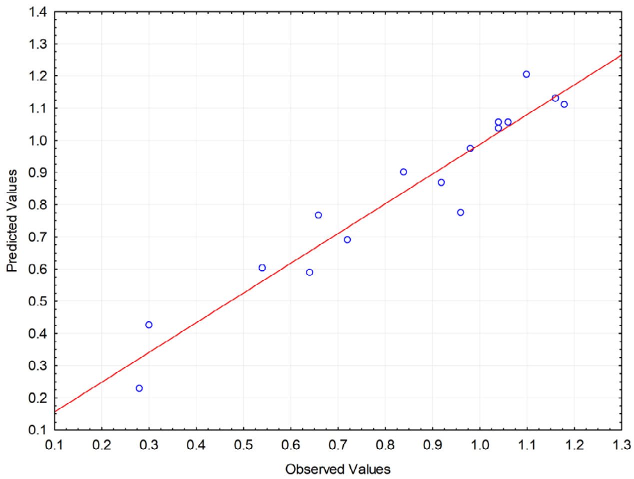

Figure 1. Correlation of predicted and observed value of KF/Ca-MgO catalyst basicity

$$Y = 1.05699 + 0.13766\,X_1 - 0.21133\,X_{12} + 0.07788\,X_2 - 0.02041\,X_{22} + 0.12708\,X_2 - 0.02395\,X_{32} - 0.0775\,X_1X_2 - 0.0225\,X_1X_3 + 0.0675\,X_2X_3 + 0.0675\,X_2X_3 \qquad (1)$$

The order of this equation is selected by correlating the coefficient of determination (R^2) for the mathematical equation is 92.37 %.This value indicates a match between the predicted value and experimental data shown in Figure 1. The linear line shown in Figure 1 is called a regression line, which indicated the best prediction between independent variables (*X*) against dependent variables (*Y*). However, it is not perfectly predictable, with a substantial reoccurring variation of the observed points around the fitted regression line (Figure 1). Residual value is defined as the deviation of a specific point from the regression line (the predicted value).

In Figure 2, the 3D surface graph shows the correlation between temperature and time of calcination, with a temperature range of 450 to 550 °C. Furthermore, it reaches the optimum basicity level, due to the temperature range of 450 to 550 °C with a change in the catalyst composition, which affects its basicity. This is by the research conducted by Xie and Huang [23] where the basicity value of the catalyst with the addition of KF on the KF/ZnO decreased after when the temperature exceeds 550 °C. The 3D surface graph in Figure 3 shows that an increase in %wt KF leads to an increase in its basicity. Therefore, its addition affects its level [24]. Figure 4 shows the correlation between the calcination time and %wt KF, which failed to contribute to the increase

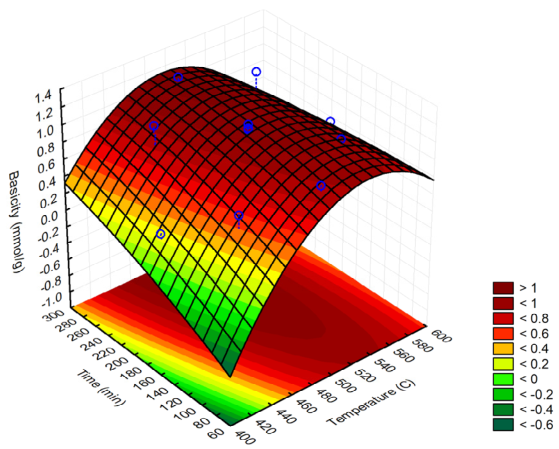

Figure 2. Surface plot of correlation between calcination time and calcination temperature on the basicity of catalysts generated at center point.

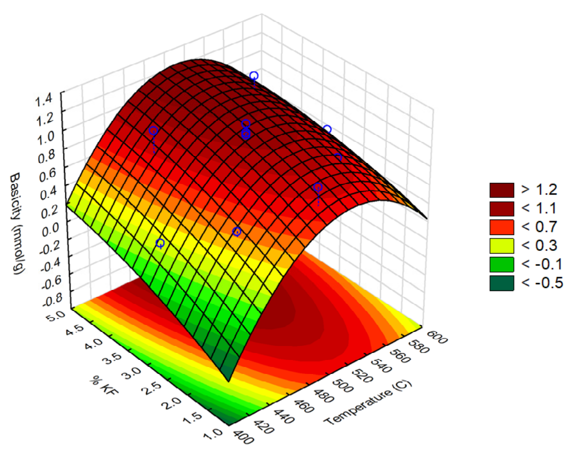

Figure 3. Surface plot of correlation between calcination temperature and %KF on the basicity of catalysts generated at center point

of catalyst basicity. The longer the calcination time, the higher the catalyst basicity value, however, it does not give a significant improvement. This shows that the addition of KF support to the CaO-MgO is the dominant factor which helps increase catalyst activity leading to higher basicity [6].

4. Conclusions

The optimized operating condition of the catalyst production is easily estimated by limiting the calcination temperature in ranges of 415.9 to 584.1 °C, the time between 1.32 to 4.68 hours, and the %wt KF content ranging from 1.3182 to 4.6818 %. This obtained an optimal catalyst basicity value of 1.18 mmol/g. The correlation between calcination temperature (X_1), calcination time (X_2), %wt KF (X_3) and the catalyst basicity (Y) is shown in Equation (1).

Acknowledgements

The authors are grateful to financial support from Indonesian Ministry of Research, Technology and Higher Education (Kemenristekdikti) under 2018 budget year.

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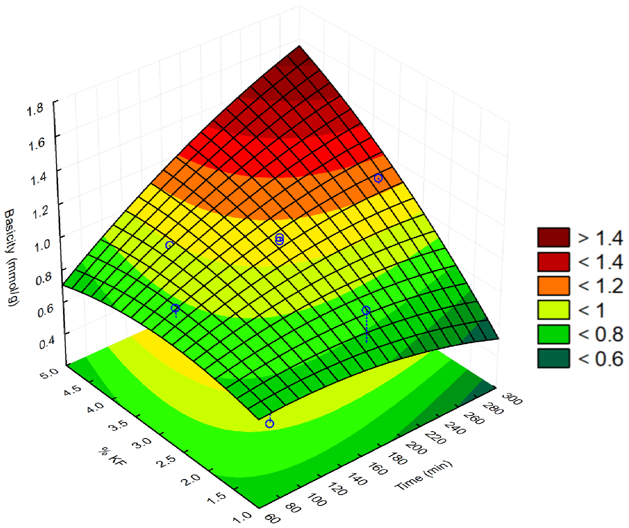

Figure 4. 3D surface of the correlation between calcination time and %KF on the performance of catalysts generated at center point

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Selected and Revised Papers from The 3rd International Conference on Chemical and Material Engineering (ICCME) 2018 (http://iccme2018.undip.ac.id) (Diponegoro University, by 19th-20th September 2018) after Peer-reviewed by Scientific Committee of ICCME 2018 and Peer-Reviewers of Bulletin of Chemical Reaction Engineering & Catalysis