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Empirical modelling of the vapour-phase dehydrogenation of ethanol using heterogeneous modified clay catalyst.

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Abstract

The empirical modeling of the vapour – phase dehydrogenation of ethanol using heterogeneous modified clay catalysts was achieved in this work. Kaolinite clay obtained from Ukpor, Anambra State was modified by thermal activation and used in the dehydrogenation reaction. Using 2^m factorial design, the effect of the process variables – process duration (x_1), catalyst weight (x_2), and reaction temperature (x_3) on the conversion was determined. Results obtained showed that the dehydrogenation reaction was effectively catalysed by the modified clay catalyst, with the catalyst weight having the greatest positive effect. The negative effect of the reaction temperature indicated the deactivation of the clay catalyst with time. The polynomial model obtained using regression analysis was deemed adequate for the description of the dehydrogenation of ethanol using the modified clay catalyst.

Keywords: Dehydrogenation; ethanol; acetaldehyde; clay catalyst; modeling; factorial design

1. Introduction

Many important reactions have been known to be catalysed by clays. The liquid phase catalytic esterification of stearic acid and vapour phase dehydrogenation of ethanol have been reported as part of a research and development series on the production of catalysts and supports from local clay resources (Igbokwe et al, 2004). Ethanol is a versatile and useful industrial solvent used as an important raw material for the production of many useful chemicals and intermediates. One major use of ethanol however is in the production of acetaldehyde. Acetaldehyde has various uses and applications and over the years a lot of effort has been geared towards its production under favourable reaction conditions.

Relatively high yields of acetaldehyde have been obtained by the oxidation and vanadium-based catalysts (Kilos et al, 2006). Vapour phase oxidative dehydrogenation on copper oxide-chromium oxide catalyst on pumice as well as over neodymium oxide or samarium hydroxide has also given yields of acetaldehyde (Kirk-Othmer, 1965). In addition, the Wacker catalyst, a homogeneous catalyst was popularly used due to the milder reaction conditions under a temperature of 130^{o}C as supposed to that used for oxidation at 500^{o}C and dehydrogenation at 250^{o}C. The production of acetaldehyde has also been achieved using silica-pillared rectorite at 390^{o}C, with 85% ethanol conversion and 80% acetaldehyde selectivity (Hao, 1994). However, large scale industrial production has so far been hindered by the performance of the available catalyst, which generally exhibits low activity and selectivity added to the high cost of regeneration and attendant environmental pollution issues.

The use of clay catalyst however provides better alternatives due to economic and environmental considerations relating to catalyst recovery (Laszlo, 1990 and Pushpaletha et al, 2005). These clay catalysts are eco-friendly and the reaction conditions relatively milder. Thus, this work investigated the effect of the reaction process variables (Catalyst weight, reaction temperature and temperature) on the dehydrogenation of ethanol using heterogeneous modified clay catalyst while obtaining an empirical model of the process.

2. Materials and methods

2.1. Clay activation

The clay sample which has been characterized to be kaolinite (Nwajagu and Aneke, 1986) was crushed and sieved. Sample with particle size in the range of -20 to +50 mesh size (particle size in the range of 0.297 – 0.841μm) was thermally activated in a furnace at 400^{o}C for four hours and used for the dehydrogenation reaction. Ethanol of analytical grade was used without further purification. A batch reactor consisting of two –

necked round bottom flask of 250cm^3 capacity, fitted with a catalyst chamber immersed in a heated sand bath at the appropriate temperature, a condenser and a sampling device was used. 100ml of ethanol was put into the two-necked flaks and heated to the appropriate temperature for the run. The vapour generated was channeled into the catalyst chamber consisting of a 40mm-diameter glass tube with a predetermined weight of catalyst immersed in a sand bath maintained at the appropriate run temperature where the dehydrogenation occurred. The product stream was subsequently condensed. Samples were drawn at time intervals and analysed using ABBE – 60 refractometer and the acetaldehyde composition determined using a calibration curve.

All the runs were carried out in a similar manner using the following ranges of process variables: catalyst loading (g) 0, 20, and 40g respectively; temperatures 200, 250, and 300^{o}C respectively. The different process variables were used in all the runs and the effect of catalyst loading, reaction temperature and process duration (min) on the dehydrogenation reaction was evaluated.

2.2. Plan of the experiment

The independent variables whose effect was investigated are as follows:

X_1 – Process duration, X_2 – Catalyst weight, and X_3 – Reaction temperature.

The actual coded values of the variables are shown in Table 1.

Table 1
Actual and Coded Values of the Independent Variables

Variables	*Actual Values*			*Coded Values*		
	Low level	Mid – Point	High Value	Low Level	Mid Point	- High Value
Process Duration (min) X_1	5	17.5	30	-1	0	+1
Catalyst weight (g), X_2	0	20	40	-1	0	+1
Reaction temperature (^{o}C), X_3	250	275	300	-1	0	+1

3. Results and discussion

The 2^3 experimental design plan and the results obtained for percentage conversion for the dehydrogenation reaction at the different levels of the variable are shown in Table 2.0. The general form of the regression model used is shown in equation 1.0.

$$Y = b + {}^{m}\sum b_i x_i + {}^{m-1}\sum \sum b_{ij}\, x_i\, x_j \quad (1)$$

Where; b_i – co-efficient of the i-th variable, x_i – i-th variable in the coded form, and m – number of variables. The expanded form of equation (1) for m = 3 is given below;

$$Y = b_o+b_1x_1+b_2x_2+b_3x_3+b_{12}x_1x_2+b_{13}x_1x_{13}+b_{23}x_2x_3+b_{123}x_1x_2x_3.$$

Table 2
Experimental design plan and results obtained for percentage conversion for the dehydrogenation reaction at different levels of variables.

S/n	X_0	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	$X_1X_2X_3$	y_1	y_2	$y_{av.}$
1	1	-1	-1	-1	1	1	1	-1	45.3	44.9	45.1
2	1	1	-1	-1	-1	-1	1	1	44.7	44.7	44.7
3	1	-1	1	-1	-1	1	-1	1	75.0	74.8	74.9
4	1	1	1	-1	1	-1	-1	-1	74.4	74.2	74.3
5	1	-1	-1	1	1	-1	-1	1	50.0	51.2	50.6
6	1	1	-1	1	-1	1	-1	-1	47.0	47.2	47.1
7	1	-1	1	1	-1	-1	1	-1	90.5	89.5	90.0
8	1	1	1	1	1	1	1	1	88.0	87.0	87.5

The regression coefficients are as determined in Table 3.

Table 3
Regression coefficients

b_o	b_1	b_2	b_3	b_{12}	b_{13}	b_{23}	b_{123}
64.275	-0.875	17.40	4.525	0.10	-0.625	2.55	0.15

Table 4
Results of Statistical Analysis of the Model

Parameter tested	Test used	Result obtained
Homogeneity of data	Cochran's Test, (G – Test)	$G_{exp} = 0.529$, $G_{cr} = 0.677$
Significance of regression co - efficient	Student's Test, (t – Test)	All co –efficients with an absolute value less than 0.2375 are insignificant
Adequacy of model	Fisher's Test, (F – Test)	$F_{exp} = 1.447$, $F_{cr} = 4.446$
Accuracy of model	Correlation co – efficient, R^2	$R^2 = 0.9998$

From the final regression equation eqn (4), it was seen that process duration negatively impacted the conversion of ethanol. This was attributed to the reduction in the effectiveness of the catalyst with time due to deactivation. However, the small value of the co – efficient indicated that catalyst efficiency was mild. The effect of catalyst weight (x_1) on conversion was most pronounced on the dehydrogenation reaction as seen from the value of the co – efficient of that variable in comparism with the other significant effect of the reaction temperature variable (x_2) and the least significant process duration variable (x_3). In addition, the combined effect of process duration and catalyst weight depicted by the interaction term (x_1x_2) was seen to be milder than the combined effect of catalyst weight and temperature (x_2x_3).

The results of the statistical analysis of the model shown in Table 4 showed that the homogeneity of the data obtained from the experiment was acceptable since $G_{exp} < G_{cr}$. The Fisher's test confirmed the adequacy of the model also in the domain of the process variables and the accuracy of the model upheld by the high value of the correlation co – efficient R^2 show that these results are corroborated or not by other works.

Conclusion

The gas – phase dehydrogenation of ethanol to acetaldehyde has been modeled in the chosen domain of three process variables – process duration, reaction temperature, and catalyst weight. It was shown that the catalyst weight had the most favourable effect on the reaction followed by reaction temperature, while the process duration had the least effect. The regression model obtained in this domain was shown to be accurate and adequately described the reaction in terms of the percentage conversion of ethanol to acetaldehyde.

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