A FACTORIAL EXPERIMENTAL DESIGN APPROACH FOR THE SYNTHESIS OF TEMPLATED ZEOLITE Y

Muhammad A. T.†, A. S Kovo‡, Makarfi Y. ‡

†Scientific Equipment Development Institute, PMB 37 Tunga goro, Minna. Niger State, Nigeria.
‡ Department of chemical Engineering, Federal University of Technology, Minna. Niger State, Nigeria. ³Cape Peninsula University of Technology (CPUT), Cape Town, Western Cape, South Africa.

*abubakartakuma@gmail.com, 08036541959.

ABSTRACT. The factorial experimental design approach for the synthesis and characterization of templated zeolite Y was carried out by the hydrothermal process procedure using high temperature, low cost chemicals and simple apparatus. Using a batch composition 23.4Na₂O: Al₂O₃: 83.4SiO₂: 4.2(C₆H₁₂N₄): 3750H₂O and structural directing agent (SDA) Hexamethylene tetramine (C₆H₁₂N₄). A ²3 fractional factorial design of experiments was applied in the design of the synthesis conditions used to conduct the experiment. The samples obtained were characterized by the use of powdered X-ray diffraction (XRD) and the scanning electron microscopy (SEM) methods. The results of the characterization showed that, the XRD patterns of the as-synthesized zeolite matched with those of the commercial Zeolite Y show sharp and narrow XRD peaks predominantly crystalline, while the images were of spherical crystals and represent a typical morphology for zeolite Y. It also showed a uniform size crystal distribution across the SEM images with an average size of 71 μm, while the highest percentage crystallinity was 48.52 %. A Mathematical model for the templated zeolite Y was derived from the experimental data and validated by the predicted and actual values of the conditions of synthesis. The optimal conditions for the synthesis of templated zeolite Y are: crystallization time of 43.00 h, crystallization temperature of 177.5 °C and ageing time of 60 h. The conditions ranges crystallization time 38-48 h, crystallization termperature 165-190 °C, while the ageing time ranges 48 -72 h. Given the results the model can be use as tool for interpretation of the obtained relationship and the conditions was validated with an R² of 0.9308 which indicates 93.08 % similarity between experimental and predicted values.

Keywords: Zeolite Y, Experimental design, Synthesis, purity.

1. INTRODUCTION

Faujasite aluminosilicate FAU, zeolite Y is a very important zeolite in respect to its volume in research activity and large scale in commercial use (Karami & Rohani, 2009). The synthetic zeolite Y has found applications principally in the field of catalytic cracking (FCC) of vacuum gasoil and in adsorption of volatile organic from wet off-gas streams (Jolanta, 2010). The faujasite materials are characterized by high surface area, uniform pore size distributions with pore sizes in the range 0.9-1.2nm and high thermal stability (Karami & Rohani, 2009).

Zeolite are generally a high class of crystalline aluminosilicate materials and the major approach to preparation of zeolite is by the hydrothermal synthesis, which is similar to the naturally occurring process that produces several classes of inorganic minerals such as crystalline silica and zeolites (Siti, 2007). Many variables mostly influence the synthesis of faujasite materials. These variables include the inorganic cations, Si/Al ratio, crystallization time and temperature, ageing time, concentration, pH, batch composition, water content (Cejka, 2007). Therefore, a multi-variable experimental design is necessary in order to investigate the factors influencing the resulting output (Dongsheng et al, 2009). To effectively synthesis Zeolite Y, mostly a single factorial method was applied to optimize the synthesis conditions, which involves varying one variable at a time and keeping the rest constant (Xiaming & Erdong, 2007). In this method, many experiments were required, and it becomes very difficult to study the interactions between the variables as they may influence the synthesis of the zeolite. Therefore, multi-variable experiment will give a better
output. It involves statistical design of experiment and it is an efficient way to obtain the maximum amount of information with fewer possible numbers of experiments, which helps in the investigation of factors influencing the resulting output (Katovic et al, 2001).

A factorial experiment can be analyzed using analysis of variant (ANOVA) or regression analysis. It is relatively easy to estimate the main effect for a factor. To compute the main effect of a factor "A", subtract the average response of all experimental runs for which A was at its low (or first) level from the average response of all experimental runs for which A was at its high (or second) level (Box & Draper, 1987).

2. METHODOLOGY

2.1 Materials

The materials used for this work are basically the reagents, which are mostly manufactured by Chadwell Heath Essay, England. The chemicals include the Aluminium Nitrate Al(NO₃)₃.9H₂O, Sodium Silicate (water glass, Na₂SiO₃.9H₂O) and a structural directing agent Hexamethylenetetramine (C₆H₁₂N₄). All the equipment were obtained in Minna and used in the Chemical Engineering Departmental laboratory, Federal University of Technology, Minna, Nigeria.

2.2 Design of Experiments

In this study, a 2³ factorial experimental design was used to determine the optimum synthesis conditions. The parameters used were the ageing time, crystallization temperature and crystallization time and were study at both low and high levels with the response been percentage purity. The high level of the ageing time was 72 h and the low level 48 h. The high level for crystallization temperature was 190 °C and the low level was 165 °C. The high level for crystallization time was 48 h, while the low level was 38 h.

<table>
<thead>
<tr>
<th>Factors</th>
<th>parameters values</th>
</tr>
</thead>
<tbody>
<tr>
<td>X₁: Ageing time (h)</td>
<td>48 72</td>
</tr>
<tr>
<td>X₂: crystallization temp (°C)</td>
<td>165 190</td>
</tr>
<tr>
<td>X₃: crystallization time (h)</td>
<td>38 48</td>
</tr>
</tbody>
</table>

The design matrix is as shown (Table 2.1).

2.3 Characterization

The phase identification was performed by X-ray diffraction (XRD) using a PANalytical X’Pert computerized diffractometer with Cu-Kα radiation (40 kV, 40 mA). The 2Θ value was scanned in a range of 5-80°. The morphology of the individual crystal was observed by scanning electron microscopy (SEM) with a PHILIPS XL-30 ESEM microscope (Dongsheng et al, 2009). The response measured, P, was the relative crystallinity of zeolite Y samples. The value of P was calculated using the following equation (Eq. (1)) from the peak area of angle 2Θ in the XRD spectra, using a highly crystalline sample

\[ \%\text{XRDcrystallinity}(P) = \frac{\sum_{\text{sample}}}{\sum_{\text{reference}}} \times 100 \]  

Where P is the relative crystallinity, \( \sum_{\text{sample}} \) sum of the peak area of product, \( \sum_{\text{reference}} \) the peak area of reference sample. While the average crystal sizes was calculated by the scanning electron micrograph (SEM) technique.

2.4 Zeolite Y synthesis procedure

A series of templated zeolites Y were synthesized hydrothermally, using salt solution of analytical Aluminum Nitrate Al(NO₃)₃.9H₂O, Sodium Silicate (water glass,
Na$_2$SiO$_3$.9H$_2$O) and a structural directing agent Hexamethylenetetramine (C$_6$H$_{12}$N$_4$). Using a batch composition 23.4Na$_2$O: Al$_2$O$_3$: 83.4SiO$_2$: 4.2(C$_6$H$_{12}$N$_4$): 3750H$_2$O. The distilled water was divided into two equal parts of 111.7 ml. The template solution was prepared by dissolving 1.95 g of Hexamethylene tetramine (C$_6$H$_{12}$N$_4$) in 111.7 ml of distilled water and stirred vigorously. The second half of the distilled water 111.7 ml was used to dissolve 2.45 g of Aluminium Nitrate Al(NO$_3$)$_3$.9H$_2$O and 88.4 g of Na$_2$SiO$_3$.9H$_2$O (water glass) sodium silicate was then added to dissolve and stirred (Tshabalala,2009).

The template solution of 111.7 ml and the second solution were then poured into a blender to stir it more intensively until a smooth jellylike form was consistently obtained. The final mixture was then transferred into 100 ml plastic beaker and allowed to age for 72 h, after which the solution was then transferred to an autoclave equipped with a 50 ml Teflon vessel. The autoclave was then put in the oven and the contents were allowed to crystallize at a temperature of 190 °C for 48 h. After the hydrothermal treatment, the autoclave contents were filtered and washed with distilled water until the filtrate had a pH of 9. The resulting product was then dried at 120 °C for 6 h and later calcined at 650 °C for a period of 4 h to get rid of the organic impurities/template. The resulting product suspected to be templated zeolite Y. Using the same procedure, the entire procedure was repeated for seven (7) different more runs for different Ageing time, crystallization temperature and crystallization time.

### 3.0 RESULTS AND DISCUSSION

The characterization of the zeolite Y produced by XRD showed that the as-synthesized zeolite Y has the characteristic peaks of zeolite Y.

The XRD patterns of the as-synthesized zeolite Y matched with known zeolite Y pattern which shows the required sharp and narrow XRD peaks (Dong, Bin, Guang, Qiang, Gaomeng, Lian and Jishuan, 2005) and are predominantly crystalline as shown in Figure 3.1. Also from Figure 3.1, the produced zeolite Y showed the characteristic peak of zeolite Y at 2θ values of 6.15°, 10.2°, 11.0° and 16.0° and there is a clear broadening of the reflection from the sample and the decrease in peak intensity from 20.2°, 30.0°. This can be attributed to the presence of small crystals and some impurities, noise and amorphous phase from 2θ values of 35° to 45°.

The XRD pattern also compared well with some other work on zeolite Y as reported in literature such as in the work of (Karami & Rohani, 2009). The percentage crystallinity which serve as the purity was calculated, is depicted in Table 3.1.
Table 3.1: Percentage crystallinity

<table>
<thead>
<tr>
<th>Run</th>
<th>Factor 1: Ageing time (hrs)</th>
<th>Factor 2: B: Cry Temp (°C)</th>
<th>Factor 3: C: Cry Time (h)</th>
<th>Response Cry (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>72.00</td>
<td>190.00</td>
<td>48.00</td>
<td>48.52</td>
</tr>
<tr>
<td>2</td>
<td>72.00</td>
<td>190.00</td>
<td>38.00</td>
<td>45.37</td>
</tr>
<tr>
<td>3</td>
<td>48.00</td>
<td>165.00</td>
<td>48.00</td>
<td>41.11</td>
</tr>
<tr>
<td>4</td>
<td>48.00</td>
<td>190.00</td>
<td>38.00</td>
<td>43.33</td>
</tr>
<tr>
<td>5</td>
<td>72.00</td>
<td>165.00</td>
<td>48.00</td>
<td>35.37</td>
</tr>
<tr>
<td>6</td>
<td>48.00</td>
<td>165.00</td>
<td>38.00</td>
<td>30.74</td>
</tr>
<tr>
<td>7</td>
<td>48.00</td>
<td>190.00</td>
<td>48.00</td>
<td>40.56</td>
</tr>
<tr>
<td>8</td>
<td>72.00</td>
<td>165.00</td>
<td>38.00</td>
<td>41.85</td>
</tr>
</tbody>
</table>

Table 3.1 shows the various percentage crystallinity at the runs conducted, the percentage is higher for the first run at 48.52% while the lowest is at run 6 at 30.74%. The percentage crystallinity is used as the response in the work and shows the purity of the synthesized zeolites (Karami et al, 2009). The Table also shows that the highest percentage crystallinity was obtained at the highest conditions of synthesis with ageing time 72 h, crystallization time 48 h and crystallization temperature 190 °C. While the lowest percentage crystallinity is at the lowest conditions with ageing time 48 h, crystallization time 38 h and crystallization temperature 165 °C respectively. This is an indication of the importance of ageing time and the crystallization time, since at highest level it gives the best results of crystallinity and at lowest the lowest respectively. But considering the factors of time and cost of running the experiment, the experimental runs 4, gives a more realistic result. The ageing and crystallization time were lower 48 h and 38 h respectively, with a corresponding temperature of 190 °C given a percentage crystallinity of 43.33% which is within the range of the experiments best. From experiment run 4, this showed that more time can be saved thereby achieving the aim at a minimum time.

The crystallite size is one of the important parameters that influence physical properties of nano-materials. Fabrication of materials with specified properties requires close control of crystallite size (Uvarov & Popov, 2006). In order to establish the crystal size of the zeolite samples, the scanning electron micrograph (SEM) technique was used. Representative micrographs of synthesized zeolites Y are shown in Figure 3.2 to 3.6 respectively.

![Fig. 3.2: SEM image of sample at Ageing time 72 h, Crystallization time 48 h and Crystallization temperature 190 °C](image)

![Fig. 3.3: SEM image of sample at Ageing time 72 h, Crystallization time 38 h and Crystallization temperature 190 °C](image)
Fig. 3.4: SEM image of sample at Ageing time 48 h, crystallization time 48 h and crystallization temperature 165 °C

Fig. 3.5: SEM image of sample at Ageing time 48 h, Crystallization time 38 h and Crystallization temperature 190 °C

From Fig. 3.2 to 3.6 an average crystal size of around 90.49 μm for microcrystalline zeolite Y image was observed and it also showed that the crystal size distribution appears to be uniform. This is expected since the precursors are protected from aggregation during the crystallization. Based on the observation from the SEM images (Fig. 3.2 to 3.6) all had similar morphology. This typical morphology for zeolite Y was shown by other researchers as well (Uvarov et al 2006).

Fig. 3.6: SEM image of sample at Ageing time 72 h, Crystallization time 48 h and Crystallization temperature 165 °C

SEM images revealed that the sample had Spherical crystals with blunt edges, and has a defined morphology of zeolite Y (Uvarov et al 2006). The crystal sizes were calculated using the SEM micro-graphs of the synthesized samples. It shows an increase in the ratios as the synthesized parameters varied.

A full factorial requires at multi level many experiments (Dongsheng et al, 2009). Interactions between different variables could be important in the study. Therefore one of fractional factorial design methods was used for the data analysis and was performed with the design Expert software version 7 (stat-Ease Inc. Minneapolis, USA), (Karami et al, 2009). The analysis of a $2^3$ factorial design resulted in an overlap between the main variables and their interaction terms. In this work, all interaction effects greater than 0.1000 were ignored. While the values lower than 0.1000 were statistically significant in the model.
Table 3.3: Analysis of variable (ANOVA for selected Factorial Model)

<table>
<thead>
<tr>
<th>source</th>
<th>Sum of square</th>
<th>df</th>
<th>Mean square</th>
<th>F-value</th>
<th>P-value</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>211.5</td>
<td>3</td>
<td>70.5</td>
<td>24.53</td>
<td>0.01</td>
<td>Significant</td>
</tr>
<tr>
<td>A-Ageing</td>
<td>29.38</td>
<td>1</td>
<td>29.38</td>
<td>13.63</td>
<td>0.03</td>
<td>Significant</td>
</tr>
<tr>
<td>B-Cry temp</td>
<td>102.7</td>
<td>5</td>
<td>20.5</td>
<td>47.66</td>
<td>0.00</td>
<td>Significant</td>
</tr>
<tr>
<td>AC</td>
<td>14.82</td>
<td>1</td>
<td>14.82</td>
<td>6.88</td>
<td>0.07</td>
<td>Significant</td>
</tr>
<tr>
<td>ABC</td>
<td>64.58</td>
<td>1</td>
<td>64.58</td>
<td>29.96</td>
<td>0.01</td>
<td>Significant</td>
</tr>
<tr>
<td>Residual</td>
<td>6.47</td>
<td>3</td>
<td>2.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor. Total</td>
<td>218.0</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Model F-value of 24.53 confirmed the model to be significant. There is only a 1.25% chance that a "Model F-Value" this magnitude could occur due to noise. Values of "Prob > F" less than 0.1000 indicated model terms are significant. In this work A, B, AC and ABC are significant model terms. Values greater than 0.1000 indicated the model terms are not significant.

Table 3.4: Calculation of the coded factors

<table>
<thead>
<tr>
<th>Factor</th>
<th>Coefficient Estimate</th>
<th>df</th>
<th>Standard Error</th>
<th>90% CI Low</th>
<th>90% CI High</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>-40.86</td>
<td>1</td>
<td>0.52</td>
<td>39.64</td>
<td>42.08</td>
<td>1.00</td>
</tr>
<tr>
<td>A-Ageing</td>
<td>1.92</td>
<td>1</td>
<td>0.52</td>
<td>0.69</td>
<td>3.14</td>
<td>1.00</td>
</tr>
<tr>
<td>B-Cry temp</td>
<td>3.58</td>
<td>1</td>
<td>0.52</td>
<td>2.36</td>
<td>4.81</td>
<td>1.00</td>
</tr>
<tr>
<td>AC</td>
<td>-1.36</td>
<td>1</td>
<td>0.52</td>
<td>-2.58</td>
<td>-0.14</td>
<td>1.00</td>
</tr>
<tr>
<td>ABC</td>
<td>2.84</td>
<td>1</td>
<td>0.52</td>
<td>1.62</td>
<td>4.06</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 3.4, showed the significant values of the coded factors, factor C is eliminated because the value of C was outside the given value of 0.1000.

Final Equation in terms of coded factors

\[ \text{Cry} \% = +40.86 + 1.92 \times A + 3.58 \times -1.36 \times A \times C + 2.84 \times A \times B \times C \]

(3.0)

Where A is the Ageing time, B is the Crystallization temperature and C the Crystallization time, respectively.

The final equation was arrived at considering the coded factors which are very significant in this work. Table 3.5, showed the diagnostic statistics of response, while Fig 3.7 is the plot of the predicted values against the actual values in the model (Eq. (3.0)).

Figure 3.7: Predicted vs Actual value

As can be seen in Figure 3.7, predicted values matched experimental (actual) values reasonably well as they converged on the linear path and the "Pred R-Squared" of 0.7890 was found to be in reasonable agreement with the "Adj R-Squared" of 0.9308 for response. Therefore this model is a sufficient basis for interpretation of the obtained relationships. The response (percentage crystallization) at any regime in the interval of our experimental design can be calculated from Eq. (3.0).

The significant nature of most of the results of experiment and interaction been significant, it can magnify or diminish the effect of a factor (Dongsheng et al, 2009). The surface plot can be visualised as a three dimensional (3D) plot that showed the predicted responses as a function of the two factors keeping others constant (Dongsheng et al, 2009).
Figure 3.8: 3D view of Interaction crystallization time against Ageing time.

The 3D plots in Figure 3.8, showed that as the ageing time and crystallization time increases, there is an increase in the percentage crystallization, until a fall is observed in percentage crystallization. While Figure 3.9, showed that the crystallization temperature and ageing time are the most important variables. This can be seen as an increase in both resulted in an increase in the percentage of crystallization.

Considering all plots of the analysis and results, the optimal condition for the synthesis of templated zeolite Y should be at a crystallization time of 43.00 h, crystallization temperature of 177.5 °C and ageing time of 60 h. The condition was validated with an $R^2$ of 0.9308 which indicates 93.08 % similarity between experimental and predicted values.

3. CONCLUSION

Synthesis of crystalline zeolite Y has been successful using hydrothermal sol gel procedure from synthesis mixtures. Zeolite Y was successfully synthesized with a single method which involved high temperatures and simple apparatus. The $2^3$ factorial design and response surface analysis are found to be efficient tools for the optimization of zeolite Y synthesis. The predicted and actual values were found to be in conformity and validated the model equation and the results showed that the model was a sufficient tool for interpretation of the obtained relationship

\[ \text{Cry} \% = +40.86 +1.92A +3.58B -1.36A*C +2.84A*B*C. \]

The optimal condition for the synthesis of templated zeolite Y should be at a crystallization time of 43.00 h, crystallization temperature of 177.5 °C and ageing time of 60 h. The condition was validated with an $R^2$ of 0.9308 which indicates 93.08 % similarity between experimental and predicted values.

ACKNOWLEDGEMENTS

The authors wish to acknowledge TETFUND Abuja for supporting this work and the contribution of Mr. Bulus Baba of Water Aquaculture and Fishery Technology, FUT Minna for his practical contribution in the course of the laboratory work.

REFERENCE


of Applied Catalysis, 55, 65-74, Doi: 10.1016/S0166-9834(00)82317-9.


