Influence of preparative conditions on the structure, acidity and catalytic activity of dealuminated Y zeolite†

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Deammoniation of NH₄Y (NH₄Y → HY + NH₃) followed by partial dehydroxylation of HY removed part of the aluminium from zeolitic framework and most of this non-framework aluminium is conveniently extracted with ethanolic solutions of acetylacetone. A series of dealuminated Y zeolite is prepared by this method varying the Si/Al ratio. These dealuminated Y zeolites are characterized by chemical analysis, XRD, BET surface area, acidity, IR, TPD of ammonia and catalytic activity in acid catalyzed reactions like cumene cracking, aniline alkylation, phenol alkylation and cyclohexanol dehydration. Shift of 1010 cm⁻¹ frequency in IR spectra to 1068 cm⁻¹ and decrease in unit cell parameter a₀ from 24.74 (NaY) to 24.32 (DHY 24) (Å) have demonstrated Na[A]₉/Cₐ₅ ≈ 12, a state of advanced dealumination. TPD of ammonia and catalytic activity over these dealuminated Y zeolites clearly show the presence of weak-moderate-strong acidity.

The dealumination of Y zeolite by thermal, hydrothermal and chemical treatments along with their characterization have been the subject of intense study. The preparation of highly dealuminated HY zeolites with SiO₂/Al₂O₃ ratios over 100 was first reported by Scherzer and followed by several other workers. The standard procedure for the preparation of Al-deficient Y zeolites involves mainly two distinct steps. In the first step, the original NH₄Y zeolite is subjected to hydrothermal treatment at high temperature. This strongly dealuminizes the zeolite framework and the vacancies created by the removal of aluminium are filled by Si atoms. In the second step the extra framework aluminium created in the first step is solubilized by acid or complexing agents. Vapour phase isomorphous substitution of aluminium is also well reported.

The catalytic properties of dealuminated zeolites are mainly governed by acid strength distribution and crystallinity which in turn depend on the framework aluminium content. Special care is, therefore, taken when the zeolite is subjected to dealumination procedure to retain the crystallinity. Thermal and hydrothermal treatments of NH₄Y can yield different products and this was extensively studied. HY zeolite is generally known to be unstable and heating above 550°C results in dehydroxylation. HY obtained in the present work is not 100% HY as there is partial collapse of the structure. Part of the framework aluminium is converted into non-framework and this non-framework aluminium is removed by solubilization with ethanolic solutions of acetylacetone. Dealuminated zeolites thus prepared are subjected to different characterization studies and the results are reported in this paper.

Experimental Procedure

The zeolite used in this work was NaY (SK 40, Si/Al = 2.42) obtained from Union Carbide. NH₄Y (Si/Al = 2.42, NH₄ exchange ≈ 90%) was prepared by four successive exchange treatments with fresh 0.5 M NH₄NO₃ solution at 80°C, washing with deionized water and drying at 120°C in air. The powder XRD pattern showed no indication of peak broadening or impurities after this exchange. NH₄Y was heated in shallow bed at 300°C for 3 h to convert NH₄Y to HY and further calcined at 550°C for 2 h.

HY then was treated stepwise with ethanolic solutions of acetylacetone (zeolite: acac = 1:1, by weight). In the first step about 50 g of HY was refluxed for 0.33 h (DHY 0.33) washed with dry ethanol, dried in oven at 100°C and further subjected to acetylacetone treatment for 1 h in the second step (DHY 1). A series of dealuminated samples DHY 0.33, DHY 1, DHY 3, DHY 6, DHY 12 and DHY 24 were prepared in this way. Thus DHY 24 is a sample treated for a total period of 46.33 h. Si/Al ratios of NaY, HY and dealuminated zeolites (DHY 0.33-DHY 24) were obtained by wet chemical analysis and sodium analyses were performed by flame photometry.

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Results and Discussion

The physical properties of dealuminated zeolites are shown in Table I. Total Si/Al ratio of the zeolite increased with dealumination. The Si/Al ratio of DHY24 shows that about 70% of aluminium is removed from HY and only 17 Al/£. are present in the final structure.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Na%</th>
<th>Si/Al ratio (bulk)</th>
<th>Al/U.C.</th>
<th>Surface area, m² g⁻¹ Cat</th>
<th>Acidity, mmole, NH₃ g⁻¹ Cat</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaY</td>
<td>10.10</td>
<td>2.42</td>
<td>—</td>
<td>594</td>
<td>—</td>
</tr>
<tr>
<td>HY</td>
<td>1.24</td>
<td>2.42</td>
<td>—</td>
<td>212</td>
<td>0.25</td>
</tr>
<tr>
<td>DHY₀.₃₃</td>
<td>—</td>
<td>4.59</td>
<td>29.62</td>
<td>319</td>
<td>0.24</td>
</tr>
<tr>
<td>DHY₁</td>
<td>1.58</td>
<td>5.14</td>
<td>26.45</td>
<td>356</td>
<td>0.30</td>
</tr>
<tr>
<td>DHY₃</td>
<td>1.64</td>
<td>6.06</td>
<td>22.43</td>
<td>484</td>
<td>0.17</td>
</tr>
<tr>
<td>DHY₆</td>
<td>1.66</td>
<td>7.15</td>
<td>19.00</td>
<td>495</td>
<td>0.15</td>
</tr>
<tr>
<td>DHY₁₂</td>
<td>1.68</td>
<td>7.81</td>
<td>17.40</td>
<td>507</td>
<td>0.12</td>
</tr>
<tr>
<td>DHY₂₄</td>
<td>1.69</td>
<td>8.00</td>
<td>17.00</td>
<td>518</td>
<td>0.12</td>
</tr>
</tbody>
</table>

X-ray diffraction patterns of the samples were recorded with a Phillips PW 1051 (CuKa) X-ray diffractometer. The degree of crystallinity of dealuminated Y zeolite was estimated in the 20 region 4-40° by comparing it to the crystallinity of the original NH₄Y form. Unit cell parameter a₀ was calculated from 20 shifts. Differential thermal analysis of dealuminated samples was carried out on a Leeds and Northrup DTA unit up to 600°C. DTA patterns of the dealuminated samples showed only one endotherm around 150°C and no other changes were observed below 600°C.

Mid-infrared spectroscopy was applied to note the changes in the zeolite structure with dealumination. Spectra were recorded using Perkin Elmer 283B spectrophotometer. The samples were in the form of wafers prepared from a mixture of 1 mg of zeolite in 300 mg of KBr. The surface area of the dealuminated zeolites was measured at 77K using nitrogen as adsorbate following the BET method. Acidity of the zeolite was determined by ammonia adsorption at room temperature by the method reported earlier. The ammonia t.p.d. measurements were carried out in a pulse reactor with a thermal conductivity detector. Helium was used as a carrier with a flow of 100 mL min⁻¹. The desorption temperature range 80-550°C was maintained linearly with a heating rate of 12°C min⁻¹. Sample(0.2 g) was pretreated for 8 h at 500°C, cooled down to 80°C and then adsorption of NH₃ was carried out at this temperature. After completion of the adsorption (1 h) the sample was purged with helium at 80°C to remove the physisorbed ammonia before starting the NH₃ t.p.d.

A fixed bed glass reactor was used for catalytic experiments. Cyclohexanol dehydration activity of dealuminated zeolites was studied at 250°C using a feed of 6 mL h⁻¹ and 3-4 L N₂ flow h⁻¹ over 0.5 g of catalyst. Cumene cracking activity was studied at 450°C using a feed of 4.5 mL h⁻¹ and 3-4 L N₂ flow h⁻¹ over 0.5 g of catalyst. Aniline and phenol alkylation reactions were studied at 400°C using a mixture of aniline-ethanol and phenol-methanol (1:5 mole ratio) feeds of 4.5 mL h⁻¹ and 3-4 L N₂ flow h⁻¹ over 0.5 g catalyst. All reactants and products were analyzed by Chemito GC on 10% SE-30 column. Aniline alkylation products were analyzed on 10% Apiezon treated with KOH.

Results and Discussion

The physical properties of dealuminated zeolites are shown in Table I. Total Si/Al ratio of the zeolite increased with dealumination. The Si/Al ratio of DHY₂₄ shows that about 70% of aluminium is removed from HY and only 17 Al/U.C. are present in the final structure.

Table I clearly shows that the surface area of HY is low compared to parent zeolite. However, surface area increased (from DHY₀.₃₃ to DHY₂₄, 319-518 m² g⁻¹) on treating HY for the removal of non-framework aluminium species. The second treatment (dehydration of HY) probably leads to the destruction of a part of the zeolite framework resulting in the formation of secondary pores. The amorphous material thus formed fills a large portion of the secondary pores. Several reports are available on non-uniform dealumination, amorphization levels, nature of extra framework phases, characterization of defects, characterization of textural properties and secondary porous structure. All these studies support the idea that with the removal of non-framework aluminium formed during hydrothermal treatments, pore volumes are increased.
Table 2—X-ray % crystallinity and unit cell constant of NaY, NH₄Y and dealuminated Y

<table>
<thead>
<tr>
<th>Sample</th>
<th>% X-ray crystallinity</th>
<th>Unit cell constant a₀, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaY</td>
<td>100</td>
<td>24.74</td>
</tr>
<tr>
<td>NH₄Y</td>
<td>100</td>
<td>24.74</td>
</tr>
<tr>
<td>HY</td>
<td>Line broadening</td>
<td>—</td>
</tr>
<tr>
<td>DHY₀.33</td>
<td>48</td>
<td>24.51</td>
</tr>
<tr>
<td>DHY₁</td>
<td>50</td>
<td>—</td>
</tr>
<tr>
<td>DHY₃</td>
<td>55</td>
<td>—</td>
</tr>
<tr>
<td>DHY₆</td>
<td>55</td>
<td>24.40</td>
</tr>
<tr>
<td>DHY₁₂</td>
<td>55</td>
<td>—</td>
</tr>
<tr>
<td>DHY₂₄</td>
<td>58</td>
<td>24.32</td>
</tr>
</tbody>
</table>

X-ray diffraction patterns of dealuminated Y zeolites are shown in Fig. 1. The diffraction of HY calcined at 550°C has shown X-ray line broadening. Heating HY above 550°C may lead to loss of Bronsted acid sites and form tricoordinated aluminium due to dehydroxylation. Aluminium in the dehydroxylated zeolite is unstable and may be removed from the zeolitic framework and remains in the zeolite cavity. X-ray line broadening in the XRD of HY may be seen as partial collapse of the zeolitic structure due to dehydroxylation. HY on treatment with ethanolic solutions of acetylacetone removed part of this non-framework aluminium: With the removal of amorphous or non-framework aluminium, concentration of crystalline portion of the zeolite increased and this is clearly seen in the XRD of DHY₀.₃₃ to DHY₂₄. Beyond 46 h treatment (DHY₁ + DHY₃ + DHY₆ + DHY₁₂ + DHY₂₄) there is no further increase in X-ray line intensity.

Several workers have reported 1-10 loss of crystallinity during thermal treatment of NH₄Y unless care is taken. When EDTA was used to remove aluminium directly from the framework, 50% aluminium was removed without appreciable loss in crystallinity 25. Later work 26 has shown that about 80% framework aluminium can be removed with EDTA while zeolite maintaining about 60-70% of its crystallinity. In the present investigation part of the framework aluminium is converted into non-framework by calcining HY above 500°C. 2⁷ Al MAS NMR studies of HY (unpublished work) clearly showed the presence of tetrahedral and octahedral aluminium along with non-framework aluminium in tetrahedral coordination. Removal of framework aluminium from the zeolite resulted in lattice contraction decreasing the unit cell parameter a₀. Several workers 27-29 have correlated the decrease in unit cell constant a₀ with Na₁Al/U.C. (number of framework aluminium atoms per unit cell) calculated either from IR spectra or Si/Al ratios of 2⁷Si NMR. From the 2θ shifts in X-ray diffraction pattern the unit cell constant a₀ is calculated. It is found that a₀ value decreased on dealumination (Table 2) i.e. from 24.74 (NaY) to 24.32 (Å) (DHY₂₄).

The mid-infrared spectra of dealuminated Y zeolites showed shifts in the characteristic asymmetric and symmetric internal as well as external vibrations (Fig. 2) as reported 18. The main characteristic position of the band around 1010 cm⁻¹, an asymmetric internal stretching vibration of TO₄ has shifted to 1050 cm⁻¹ in air calcined NH₄Y (HY) and 1068 cm⁻¹ in highly dealuminated zeolite sample (DHY₂₄). Since O-T-O (T = Si or Al) stretching frequencies increase with decreasing aluminium content in zeolite structure, it is also possible to calculate from IR characteristic stretching vibration, the Na₁Al. It has been demonstrated that shifting of IR absorption bands in the 800-1050 cm⁻¹ region in a linear manner as the number of aluminium atoms per unit cell, varied in a series of aluminium deficient zeolites 3⁰. In the absence of NMR data, it is not possible to distinguish between total and
framework aluminium. However, a linear relation has been shown between $N_{AI}$ and unit cell size and also $N_{AI}$ and IR stretching vibrations. 

An attempt has been made to fit the data (Table 3) in the linear relation. The band around $1010$ cm$^{-1}$ of NaY is shifted to $1050$ cm$^{-1}$ (HY) on deammoniation and calcination indicating the removal of aluminium from the framework. From $^{27}$Al NMR results (unpublished work) the calculated $N_{AI}$ (framework aluminium, $N_{AI} = 37$) of this sample is higher for this shift.

For highly dealuminated samples DHY$_{12}$ and DHY$_{24}$ the values fit exactly in the relation $N_{AI}$ vs IR stretching bandwidth $1050$ cm$^{-1}$. That is 11 to 12 aluminium atoms in the framework correspond to a stretching frequency of $1068$ cm$^{-1}$. In the same way the decrease in the unit cell constant $a_0$ also fits in the relation very well for the highly dealuminated samples. $12$Al (framework $N_{AI}$/U.C. correspond to a decreased value of unit cell constant $24.32$ Å). The slight variation that is observed at the initial stages of dealumination may be due to deammoniation and dehydroxylation and the presence of aluminium in more than three forms (tetrahedral Al, octahedral Al, non-framework tetrahedrally bound aluminium and amorphous aluminium).

The t.p.d. curves for the desorption of ammonia from HY and dealuminated Y zeolites (DHY$_{0.33}$-DHY$_{24}$) are shown in Fig. 3. In the case of HY and DHY$_{0.33}$ only one broad NH$_3$ desorption peak is observed whereas on DHY$_1$ to DHY$_{24}$ a low temperature peak and a high temperature peak are clearly seen. The coverage of first peak increased and the coverage of the second peak remained almost same from DHY$_3$ to DHY$_{24}$. $T_{max}$ of first peak shifted from $204°C$ (DHY$_{0.33}$) to $132°C$ (DHY$_{24}$) whereas $T_{max}$ of second peak did not change much and remained around $450°C$.

Corma et al.$^{31}$ compared the information obtained by ammonia t.p.d. and pyridine adsorption-desorption on the acidity of dealuminated HY zeolites. They assigned peak 1 to ammonia adsorbed by sites with 0, 1 and 2 aluminium in the second coordination sphere (i.e., Si surrounded by 0, 1 and 2 aluminium) while peak 2 to ammonia adsorbed on sites with 0 and 1 aluminium in the second coordination sphere. They also concluded that acid centres titrated by ammonia t.p.d. up to $550°C$ correspond to 0 and 1 aluminium sites irrespective of the method of dealumination.

Dima and Rees$^{32}$ also report two peaks in the t.p.d. of ammonia over dealuminated HY. They ascribed low temperature peak to physisorbed ammonia. Choudhary et al.$^{33}$ reported the stepwise thermal desorption of ammonia in number of steps from $130-700°C$. Their results indicate that zeolites have a broad site energy distribution and differ widely in their acidity. In the present course of investigation presence of a broad NH$_3$ desorption peak on HY and DHY$_{0.33}$ ($120-500°C$) is showing broad distribution of acid sites. Splitting of this broad peak into a low temperature peak (with more coverage) and a high temperature peak (with less coverage) may be indicat-
Table 4—Product distribution (%) in acid catalyzed reactions over dealuminated Y zeolites

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Cyclohexanol dehydration</th>
<th>Cumene cracking</th>
<th>Aniline alkylation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cyclohexanol</td>
<td>Benzene</td>
<td>Ethylbenzene</td>
</tr>
<tr>
<td>NaY</td>
<td>75.0</td>
<td>96.4</td>
<td>Traces</td>
</tr>
<tr>
<td>HY</td>
<td>96.6</td>
<td>94.7</td>
<td>3.7</td>
</tr>
<tr>
<td>DHY0.33</td>
<td>94.6</td>
<td>93.3</td>
<td>3.3</td>
</tr>
<tr>
<td>DHY1</td>
<td>43.2</td>
<td>93.2</td>
<td>0.1</td>
</tr>
<tr>
<td>DHY3</td>
<td>17.1</td>
<td>93.4</td>
<td>0.2</td>
</tr>
<tr>
<td>DHY6</td>
<td>15.1</td>
<td>93.3</td>
<td>3.3</td>
</tr>
<tr>
<td>DHY12</td>
<td>15.2</td>
<td>93.7</td>
<td>3.2</td>
</tr>
<tr>
<td>DHY24</td>
<td>3.0</td>
<td>94.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Acidity and catalytic activity of dealuminated zeolites are shown in Tables 1 and 4. Total acidity measured by NH3 desorption increased on dealumination showing maximum at DHY1 and then decreased. Acidity did not differ from DHY3 to DHY24 as the dealumination process after DHY3 is very slow. Removing more than 1/3 of aluminium from Y zeolite affects the strong acidity and thus the catalytic properties. Removal of 2/3 aluminium from Y zeolite is a state of advanced (high) dealumination.27Al MAS NMR spectra of HY showed the presence of tetrahedral and octahedral aluminium along with non-framework aluminium in tetrahedral coordination (AlOOH) (unpublished work). It is this non-framework aluminium in tetrahedral coordination that disappeared (DHY3-DHY12) with acetylacetone treatment and appeared again (DHY24) on prolonged treatment. The nature of acidity associated with the framework aluminium and non-framework aluminium may be understood to some extent through acid catalyzed reactions. To explore the type and nature of acid sites, cumene cracking, aniline alkylation, cyclohexanol dehydration and phenol alkylation activities are studied. The product distribution in the first three reactions are given in Table 4. The main products of cumene cracking are benzene and ethylbenzene. N-ethyl and N,N'-dicthylanilines are the major products of aniline alkylation along with C-alkylated anilines in trace amounts. Cyclohexene is the only product in cyclohexanol dehydration activity. No considerable phenol alkylation activity is observed (<2%). A maximum of 7% cumene cracking activity is observed on DHY1 and acidity measured by NH3 is maximum on this zeolite. Maximum aniline alkylation activity (20% conversion) is also observed on DHY1. Earlier studies reported a decrease in cumene cracking activity over aluminium deficient zeolites with very high SiO2/Al2O3 ratios34. Aniline alkylation activity on HZSM-5 with SiO2/Al2O3 = 30 is low and high activity is observed35 on HZSM-5 with SiO2/Al2O3 ratio > 70. Studies on effect of pretreatment temperature on acidity and aniline alkylation activity over HZSM-5 with SiO2/Al2O3 ratio 30-280 clearly demonstrated that aniline alkylation activity is associated with Bronsted proton36. Same levels of cumene cracking and aniline alkylation activities are observed from DHY1 to DHY12. This may be seen as the type and nature of the acid site involved in both the reactions is same. Phenol alkylation activity which is less than 2% on all the dealuminated zeolites indicates that this reaction is not favoured by the type of acid sites available.

The dehydration of cyclohexanol has been demonstrated as a test reaction for zeolite acidity37. Results obtained in cyclohexanol dehydration activity over dealuminated zeolites are interesting and differ from that of cumene cracking and aniline alkylation activities. Cyclohexanol dehydration activity increased with increasing total Si/Al ratio showing maximum conversion (97%) on DHY24 (Fig. 4). Thermal dealumination will tend to decrease the effective pore diam-
eter by generating amorphous material in the zeolite channels and thus increases the resistance to diffusivity. Increase in cyclohexanol dehydration activity may be seen as low diffusion resistance of the aluminium deficient zeolites that might have resulted from the removal of amorphous material from the zeolite channels making the acid sites available. To understand further the nature of acid sites this reaction was studied for more than 5 h over these dealuminated zeolites (Fig. 5). These results indicate that highly dealuminated Y zeolites have acid sites suitable for cyclohexanol dehydration.

**Conclusion**

Heating HY at 550°C resulted in partial collapse of the zeolite due to dehydroxylation. Most of the non-framework aluminium formed during this treatment is removed on treating it with ethanolic acetylated. Dealuminated zeolite prepared by this method showed all characteristic XRD lines of the parent zeolite. Increase in surface area, shift in the IR stretching frequency at 1010 cm⁻¹ and decrease in the unit cell constant, all the characteristics of dealuminated Y zeolites are exhibited by these samples. Removal of 2/3 aluminium content from the zeolite is a state of advanced dealumination where strong acidic properties are minimum. However, typical acid site strength distribution is obtained from DHY₃ to DHY₂₄ (Al/U.C. = 22.43 to 17.0) where maximum cyclohexanol dehydration activity is shown.

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**References**