One step syntheses of zinc exchanged 4A and P zeolites from metakaolinite

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Calcination of kaolinite at 750°C results in metakaolinite (MK). Hydrothermal digestion of a slurry of MK and zinc oxide at ~120°C results in the formation of zinc exchanged zeolite A in a single step. Addition of silica to the above system and digestion results in zinc exchanged zeolite P. Thus, syntheses of two types of zinc exchanged zeolites are obtained from clay.

Basic zinc carbonate and zinc exchanged salts release zinc ions and these possess antimicrobial properties especially as mouth-wash products. In view of this, zinc zeolites were considered to be important and hence, the present investigation was undertaken.

Zeolites in sodium form are converted into metal ion-exchanged zeolites by treatment with the salt of the desired metal ion, e.g., in the case of Zn A preparation. 4A zeolite is treated with ZnCl₂ solution. But this is a cumbersome two-step process. Incorporation of Zn in the zeolite framework in one step has been described from silica (Ludox AS 40), NaOH, aluminium sulphate, zinc sulphate and tetramethylammonium hydroxide at 170°C in 72 hr. The presence of tetraalkyl ammonium template facilitates the zinc substitution in framework. These reagents are costly and we wanted to explore the possibility of syntheses in a single step through activated clay route at much lower temperature in the absence of a template. One of the objectives of the present investigation is the synthesis of Zn A in one step by making use of metakaolinite (MK).

Clays are naturally occurring aluminosilicates and they can be converted into zeolites by suitable thermal/chemical treatments. Typically hydrothermal digestion of clays (kaolin, bentonite and pyrophillite) at higher (> 4N) concentrations of caustic soda results in the formation of sodalite octahydrate (viz. Na₄(AlO₂)₁₂(SiO₂)₆.8H₂O.2NaOH). On the other hand, when clays are suitably treated and digested at lower concentrations of caustic soda (~2N), zeolite 4A (viz. Na₁₂(AlO₂)₆(SiO₂)₆.27H₂O) is formed. Thus, kaolinite upon calcination (at 750°C for 2 hr) gives metakaolinite, which gets converted into 4A by the subsequent hydrothermal treatment at ~95°C for ~3 hr in 2 N NaOH.

Gismondine (GIS) is another novel zeolite with high calcium exchange capacity. It is a family of zeolites called zeolite P with the general formula Na₆(AlO₂)₆(SiO₂)₆.15 H₂O. Structurally, the difference between P and 4A lies in the extent of zeolitic water and the silica:alumina ratio. It appeared possible to influence the formation of the type of zeolites (4A or P) by merely changing this ratio. Silica supplementation to an otherwise 4A zeolite forming system should result in P type product. The current study investigates this possibility of synthesising Zn P in a single step using MK.

Materials and Methods

MK was prepared by calcining kaolinite (ex. English India China Clay, Trivandrum) in a muffle furnace at 750°C for 2 hr. Disappearance of the XRD fingerprints of kaolinite (12.5 and 25, °2θ) and the FTIR hydroxyl frequencies (at 3695(s), 3719(s), 3670(w) and 3653 (w) cm⁻¹) demonstrated
Table 1 — Synthesis of zinc zeolites

<table>
<thead>
<tr>
<th>Batch No.</th>
<th>NaOH(g)</th>
<th>Al source(g)</th>
<th>SiO2 (g)</th>
<th>MK(g)</th>
<th>ZnO(g)</th>
<th>H2O(ml)</th>
<th>Temp(°C)</th>
<th>Period(hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>8.6</td>
<td>15.4</td>
<td>48</td>
<td>-</td>
<td>1.1</td>
<td>220</td>
<td>90</td>
<td>96</td>
</tr>
<tr>
<td>B2</td>
<td>8.6</td>
<td>15.4</td>
<td>48</td>
<td>-</td>
<td>1.1</td>
<td>220</td>
<td>90</td>
<td>96</td>
</tr>
<tr>
<td>B3</td>
<td>16</td>
<td>6.64</td>
<td>31.8</td>
<td>-</td>
<td>1.2</td>
<td>145</td>
<td>90</td>
<td>110</td>
</tr>
<tr>
<td>B4</td>
<td>28</td>
<td>17.68</td>
<td>58</td>
<td>-</td>
<td>4.1</td>
<td>112</td>
<td>90</td>
<td>102</td>
</tr>
<tr>
<td>B5</td>
<td>70</td>
<td>-</td>
<td>145</td>
<td>-</td>
<td>10.2</td>
<td>530</td>
<td>128</td>
<td>9, 92</td>
</tr>
<tr>
<td>B6</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>35</td>
<td>6</td>
<td>500</td>
<td>120</td>
<td>6</td>
</tr>
<tr>
<td>B7</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>35</td>
<td>6</td>
<td>500</td>
<td>120</td>
<td>12</td>
</tr>
<tr>
<td>B8</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>35</td>
<td>6</td>
<td>500</td>
<td>120</td>
<td>48</td>
</tr>
<tr>
<td>B9</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>35</td>
<td>6</td>
<td>600</td>
<td>120</td>
<td>24, 48</td>
</tr>
<tr>
<td>B10</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>35</td>
<td>12</td>
<td>600</td>
<td>120</td>
<td>6, 16</td>
</tr>
<tr>
<td>B11</td>
<td>30</td>
<td>-</td>
<td>20</td>
<td>35</td>
<td>12</td>
<td>600</td>
<td>120</td>
<td>5, 24</td>
</tr>
</tbody>
</table>

the completion of conversion of kaolinite into metakaolinite. The mass loss by TGA was 13.9% due to dehydroxylation around 520°C.

Standard samples of 4A (Weissalith P ex. Degussa) and P zeolites (ex. Crosfield) were also used for reference. AR grade ZnO was used in this study.

Synthesis
Most of the experiments were conducted in a one litre Parr autoclave at 120 ± 1°C and the autogenous pressure (~ 20-25 psig was registered). The charges used are listed in Table 1. The reaction was conducted for a known period of time and contents were cooled. A representative sample was withdrawn periodically and the autoclave was reassembled and the reaction continued. The samples were washed with water by reslurrying, dried (at 110°C) and ground using a pestle and mortar.

Characterisation of zeolites
The zeolite samples were examined by the XRD technique using a Siemens Kristalloflex Diffractometer. Nickel filtered copper K-alpha radiation was used. For confirming the absence of octahedral aluminium in the samples of zinc zeolites, 27Al MAS NMR technique was employed. Three representative zeolites were examined using Varian 300 MHz machine at the Regional Sophisticated Instrumentation Centre (Mumbai).

Determination of zinc in the zeolites
Under hydrothermal conditions, ZnO forms sodium zincate solution through zinc hydroxide. Zinc can get incorporated into the zeolite samples through physical entrainment, occupying framework position or exchange sites.

However, entrained zinc ions are soluble in alkali solution. As the medium is alkaline, the entrainment will be minimal. The caustic treated extracts were subsequently titrated with 0.1M EDTA solution. Eriochrome Black-T and Xylenol Orange were used as indicators in the titration. Zinc present in the exchange sites and framework can be leached out with acids and estimated by EDTA titrations. For this determination, 1 g of the
zeolite sample was digested with 5 ml of H₂SO₄ (taken in 50 ml of water). The solids were separated and the filtrate was made upto 100 ml. A known aliquot of the solution was estimated for Zn²⁺ content by EDTA titrations. Each ml of 0.1M EDTA corresponds to 7.538 mg of Zn²⁺.

Particle size
A few representative samples were examined for the size distribution by using Coulter Multisizer II.

Calcium exchange capacity (CEC)
The CECs of 4A and P (SiO₂/Al₂O₃:2) are about 280 and 276 mg of CaCO₃ per g of anhydrous zeolite. If the zeolites are already exchanged with Zn²⁺, the experimentally observed value will be smaller than the theoretically anticipated value. The CECs were determined by the EDTA titration using Ca²⁺ hard water. The drop in Ca²⁺ level of water due to the addition of zeolite is determined and reported on the anhydrous basis in this study.

Nature of the residue after acid leaching
Acidification of the zeolites to ~ pH 5 by citric or acetic acid followed by digestion at 90°C showed the extractability of Zn²⁺ from the exchange positions. Acid-treated, washed and dried zeolites were subjected to XRD analysis with a view to identifying whether there was any loss in the crystallinity. Such loss will suggest the presence of zinc in the framework position.

SEM studies
SEM examination of three representative zeolite samples was made with a Hitachi S570 machine. The shapes / sizes could be arrived at from this study.

Results and Discussion
XRD fingerprints and the FTIR studies confirmed that the samples were pure. Chemical analysis of kaolinite (SiO₂ 44.3%, Al₂O₃ 42.3%, Fe₂O₃ 0.37 and H₂O 13.9%) also suggested that the sample was of good purity.

Zeolite synthesis
Heating aluminate/aluminium hydroxide, sodium hydroxide, silica, zinc oxide and water (Table 1) at 90°C for periods upto 110 hr did not produce any zeolite. Raising of temperature led to the formation of zeolite. In view of this, the synthesis was undertaken at ~120°C under stirring with a charge of 44.2 g Al(OH)₃, 145 g of SiO₂, 70 g of NaOH, 10.2 g of ZnO and 530 ml of water (Batch No. 5). In this preliminary investigation, XRD showed formation of zeolite P at 9 and 50 hr of hydrothermal treatment (Fig. 1). Zeolite P thus formed has a tendency to undergo certain structural changes when the process extends for longer time [see Fig. 1 curve for B 5 (92 hr)]. Such changes were also noticed when zeolite P solid was heated at higher temperatures.

Zn A from MK
MK is an activated clay wherein T-Os are already linked. When it was digested with caustic soda solution (~ 1.5±0.5N) 4A formation occurred. To enable the formation of zeolite and zinc exchange to take place in one step, a higher temperature (128°C) was selected. Three batches were investigated at 1.5N NaOH with 35 g MK, 6 g ZnO and 500 ml water. Hydrothermal digestion periods were changed with this charge (In batch 6, 5 hr; batch 7, 12 hr and batch 8, 48 hr). The XRD patterns obtained with these products are
presented in Fig. 2. Some physico-chemical characteristics of the zeolites are presented in Table 2. XRD fingerprints of these samples matched well with those of 4A. The pH of a 2% slurry was in the range of 9.7 to 10.1. The particle sizes were in the range of 7.4 to 30μ. The CEC of the samples was 205 mg of CaCO₃/g of zeolite. The zinc level varied from 0.2 to 13.6% in these zeolites. The zinc levels in the 6 hr batch (batch 6) was 0.2% and in the 12 hr batch (batch 7) it was 13.6%. The crystallinity in the 6 hr batch was similar to that in 12 hr or 48 hr batch generally. This appears to suggest that 4A is first formed and Zn²⁺ exchanges subsequently.

Synthesis of P using MK

The silica/alumina ratio in MK is 2. In 4A also it is 2. As this ratio for the reactant and product matched, 4A synthesis occurred. In the case of P zeolite, however, the ratio of silica/alumina varies between 2 and 5. Supplementation of silica in a 4A-forming system should produce P zeolite. In batch No. 9, 20 g of SiO₂ was included and hydrothermally digested for 24 and 48 hr. The resulting samples showed the formation of P zeolite as expected (Fig. 3). The zinc level in the product was 7.9%.

In another batch (11), the zinc oxide level was doubled (12 g) and the other conditions were kept the same as in batch 9. P formation occurred with this extra zinc oxide charge. The zinc level had increased to 15.1%. As the zinc level increased from 7.9% (batch 9) to 15.1% (batch 11), the CEC dropped from 205 to 170 mg CaCO₃/g of zeolite. This indicates that the zinc ion substitution has a sieving effect on the Ca²⁺ ion exchange.

The concentration of caustic soda used influences the type of zeolite formed. In the earlier studies at ~95°C, 4A was formed under low (1-2N) caustic soda levels, whereas at 4N and higher levels sodalite octahydrate was produced. We wanted to examine the influence of dilution at higher temperatures (~128°C) on this system. The NaOH level in batches 6,7 and 8 was taken as reference point (30 g NaOH, 35 g MK and 6 g ZnO). In the batch 10, 20 g caustic soda, 35 g MK and 6 g zinc oxide were charged. The zeolitisation resulted in formation of P type zeolite (Fig. 4). It is surprising that lowering of the caustic soda concentration facilitates P zeolite formation.

Table 2 — Characteristics of zeolites

<table>
<thead>
<tr>
<th>Batch No.</th>
<th>pH (2% slurry)</th>
<th>Nature of the zeolite</th>
<th>psd (μm)</th>
<th>CEC mg CaCO₃/g</th>
<th>Zn content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B5</td>
<td>9.42</td>
<td>P-type</td>
<td>-</td>
<td>45</td>
<td>3.02</td>
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<tr>
<td>B6</td>
<td>9.87</td>
<td>A</td>
<td>9.85</td>
<td>205</td>
<td>0.19</td>
</tr>
<tr>
<td>B7</td>
<td>10.05</td>
<td>A</td>
<td>29.9</td>
<td>205</td>
<td>13.57</td>
</tr>
<tr>
<td>B8</td>
<td>9.65</td>
<td>A</td>
<td>7.36</td>
<td>205</td>
<td>7.54</td>
</tr>
<tr>
<td>B9</td>
<td>10.51</td>
<td>P-type</td>
<td>11.79</td>
<td>205</td>
<td>7.91</td>
</tr>
<tr>
<td>B10</td>
<td>9.71</td>
<td>P-type</td>
<td>11.79</td>
<td>195</td>
<td>6.78</td>
</tr>
<tr>
<td>B11</td>
<td>10.45</td>
<td>P-type</td>
<td>10.85</td>
<td>170</td>
<td>15.08</td>
</tr>
</tbody>
</table>
Thus, at 128°C, mere incorporation of SiO₂ generates zeolite P and lowering of caustic soda concentration alters the selection of zeolite (from 4A to P). Presence of a prominent peak at 550-560 cm⁻¹ (in FTIR) in the zeolites is due to the formation of 4A. This is very weak in P zeolites. There is also collaborative evidence from the XRD findings.

ZnO shows the d values of 1.63, 1.9, 2.48, 2.60 and 2.81 Å. These fingerprints were not observed in the zeolite sample prepared by us which clearly indicates that Zn is in the exchange sites.

*SEM studies*

4A formation with MK showed sharp cubic crystals at ~90°C. However, the zinc exchanged zeolites (A and P types) showed large spherulitic crystallites.

*Location of Zn²⁺*

ZnO was absent in the zeolites synthesised. Entrained Zn²⁺ was also minimal (≤ 0.2%). Zn²⁺ displacement due to acid treatment was almost complete. Upon treatment with organic acids (pH 5) and subsequent washings, the X-ray pattern remained nearly similar to the original. There was only a marginal loss in crystallinity. This indicates that the Zn²⁺ is extractable by H⁺ ions and hence Zn²⁺ ions are not present in the framework and are in the exchange positions. This suggests that the products obtained are Zn A and Zn P.

²⁷Al MAS NMR (Fig. 5) has shown the presence of Al in the tetrahedral coordination state, revealed by the peak at ~ 58 ppm with respect to [Al(H₂O)₆]³⁺ at 0 ppm. This clearly suggests the absence of Al with six coordination number (and hence elsewhere suggested possibility of rehydration of metakaolinite does not seem to
occurs). If Zn ions were present in the framework, the CEC would have been theoretically much higher than 280 mg CaCO₃/g. In the present case, the increase in Zn level decreases the CEC suggesting the absence of zinc in framework.

The antimicrobial efficacy of the zinc exchanged zeolites will be examined in due course.

**Conclusion**

By reacting metakaolinite, sodium hydroxide and zinc oxide, both Zn A and Zn P zeolites could be synthesised in a single step at ~120°C. It appears that 4A is formed initially and gets exchanged with Zn²⁺ *in situ* subsequently. By adding higher levels of silica to the above Zn A forming recipe, Zn P is formed. Use of dilute caustic soda also leads to the formation of Zn P. Zn²⁺ ions are found to be in the exchange sites as reflected from the studies made by exchanging the products with H⁺ and Ca²⁺ (EC); XRD and $^{27}$Al MAS NMR.

**References**