Treated fly ash: A potential catalyst for catalytic cracking

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Fly ash from a Thermal Power Plant was converted to zeolite by alkali fusion followed by hydrothermal treatment. The formation of zeolite was confirmed by X-ray diffraction and scanning electron microscopy. The performance of the prepared zeolite as cracking catalyst was tested by carrying out cracking of a heavy crude residue. Cracking of the same feed was also carried out with raw (untreated) fly ash and commercial 13X zeolite. At 11 wt% catalyst loading, temperature 380°C and atmospheric pressure, the feed conversions to lighter products (bp ≤ 250°C) obtained were 35.6%, 58% and 58% with raw fly ash, treated fly ash and commercial zeolite, respectively, as the catalyst.

Large numbers of coal fired power plant all over the world dispose a huge quantity of fly ash causing a serious environmental problem. Less than a half of the ash is used as a raw material for concrete manufacturing and construction; the remaining being directly dumped on land side as landfill or simply piled up. Due to shortage of landfill sites and tighter environmental regulations, new ways of utilizing fly ash are needed. Because of the presence of SiO₂ and Al₂O₃ in high proportions in fly ash, it can be converted to crystalline aluminosilicates or zeolites. Due to their uniform pore size and large surface area, zeolites are widely used as adsorbent and catalyst for various processes. The present work is concerned with the preparation of zeolite catalyst from coal fly ash suitable for catalytic cracking.

Catalytic cracking has now become the heart of the modern petroleum refineries. Its importance is ever increasing due mainly to its flexibility in treating a wide variety of feed stocks. This flexibility is most desired in refineries as refiners are obliged to resort to heavier crudes containing refractory and/or poisonous constituents because of shortage and consequent high price of more desirable feed stocks.

In catalytic cracking, catalysts are used to get more valuable and selective products. Typically, zeolite-type catalysts are used with better yields and selectivity. However, zeolites are very costly and the economics of the process mostly depend on proper regeneration of catalyst for reuse. Research work is going on to find alternative catalyst of low cost, but of similar performance as zeolite catalysts. The objective of this study is to prepare a low-cost cracking catalyst from fly ash by hydrothermal treatment and testing the activity of the catalyst by carrying cracking reactions with a heavier feedstock.

Zeolites from Fly Ash

Coal ash is composed mainly of some oxides derived from inorganic compounds which remain after burning. The amounts of the main components of the ash, i.e., SiO₂ (40-65%) and Al₂O₃ (25-40%), show few variations with the type of coal. As minor components, Fe₂O₃ (5-10%) and oxides of Ca, Mg, Ba, P, Ti, etc. (trace) are also included in the ash. With silica and alumina as the major constituents, the fly ash is a very good starting material for zeolite.

Several methods have been reported in the literature for the preparation of zeolite from fly ash. Attempts have been made to convert the whole of the fly ash particles into zeolite by alkali fusion prior to hydrothermal treatment. Several researchers have synthesized zeolite from fly ash for cation exchange applications. Lin and Hsi have synthesized zeolite like material from fly ash having cation exchange capacity. They have evaluated different hydrothermal conditions for achieving maximum cation exchange capacity of the synthesized zeolite. Fly ash has also been converted to zeolites as ion exchangers in waste treatment applications. Zeolite material has also been synthesized from fly ash by microwave assisted alkaline activation. Synthesis yields and zeolite types obtained from microwave assisted treatment has been reported to be very similar to that obtained from conventional hydrothermal treatment. Successful synthesis of zeolite from Class F fly ash and sodium aluminate has also been reported in the literature. The reaction has been studied as a function of composition, time and temperature.

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From the above discussion, it is evident that fly ash can be converted to zeolite for various applications like ion exchange, waste treatment, etc. There is, however, no information in the literature on the application of fly ash or treated fly ash as catalyst for cracking reactions. With the high silica and alumina content of fly ash, it was thought desirable to explore the ability of fly ash and/or treated fly ash as cracking catalyst.

**Experimental Procedure**

*Preparation of zeolite from fly ash*—The fly ash used in this study was obtained from Kolaghat thermal power plant, West Bengal, India. The composition of the fly ash used is given in Table 1. In the preparation of zeolite, the method developed by Shigemoto et al. was used with some modification. A mixture of 120 g of sodium hydroxide and 100 g of fly ash were milled and then heated in a tray at 500°C for 1 h. The resultant fused mixture was cooled to room temperature, milled again, mixed with 1 L of water and then agitated mechanically for 12 h. The slurry was then kept at around 90°C for 6 h without stirring. The precipitates were filtered, washed repeatedly with water and dried overnight at 100°C.

*Characterization of zeolite*—Powder X-ray diffraction (XRD) pattern for the various samples were obtained using CoKα radiation by using Phillips BW1710 automated power diffractometer. The diffraction pattern of the treated and untreated fly ash were taken and compared with XRD pattern of typical 13X (NaX) zeolite. The formation of zeolite by treating fly ash hydrothermally was thus confirmed from this comparison as evident in Fig. 1. Compositions of the samples under experiment were determined with the help of Scanning Electron Microscope (Model: JEOL, JSM 5800). The compositions of treated fly ash and commercial 13X zeolite are also shown in Table 1. The scanning electron micrographs (SEM) of different samples are shown in Fig. 2. The SEM of raw fly ash (Photo 2a) showed a mixture of amorphous spherical particles of different sizes. The SEM of treated fly ash (Photo 2b) showed the change of amorphous nature of the raw fly ash to crystalline nature and the structure is similar to that of commercial 13X zeolite (Photo 2c). Large spherical structure of fly ash was transformed into three-dimensional sieve structure that aggregated to form the irregular forms in their shapes. Mainly

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Fly ash</th>
<th>Treated fly ash</th>
<th>13X Zeolite</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>55.19</td>
<td>43.81</td>
<td>48.26</td>
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<tr>
<td>Al₂O₃</td>
<td>31.91</td>
<td>28.56</td>
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<td>Fe₂O₃</td>
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<td>TiO₂</td>
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<tr>
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<td>0.79</td>
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</tr>
<tr>
<td>BaO</td>
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<td>Na₂O</td>
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<tr>
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<tr>
<td>SO₃</td>
<td>0.00</td>
<td>0.00</td>
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Fig. 1—X-ray diffraction patterns of fly ash, treated fly ash and 13X zeolite.
hexagons of almost uniform size and surfaces are found embedded in large matrix-like structure. However, the presence of inter-growth in the crystal makes it difficult to define an average particle size and actual structure of a crystal. From the XRD pattern, it is evident that the crystallinity of the fly ash, which is amorphous in nature, is changed very much.

Testing of catalyst activity—The activity of the prepared zeolite (treated fly ash) was tested by carrying out cracking reaction with a heavier fraction of North Gujarat (India) heavy crude. For a typical run, about 250 mL of heavy oil was refluxed with 11 wt% catalyst for a fixed period of time and the cracking reaction was allowed to proceed at a constant temperature. After the reaction, the catalyst was separated from the reaction mixture and the components boiling below 250°C were removed from the mixture. The residue volume was noted.

Results and Discussion

The cracking operation was carried out with the catalyst prepared from fly ash. The cracking feedstock used for this study was the heavier fraction of North Gujarat crude. It was having a boiling point of 300°C+ and an API gravity of 24°. To compare the activity of the prepared catalyst, cracking was also carried out with commercially available 13X zeolite as well as with raw fly ash. The cracking reaction was carried out at an average temperature of 380°C for 4 h and the lighter products produced by cracking were condensed and collected. The feed conversion was calculated from the volume and specific gravity of the collected products. For this, the conversion was defined as the volume per cent of the feed which disappeared to form products boiling below the

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Fig. 2—Scanning electron micrographs of fly ash, treated fly ash and 13X zeolite.

Fig. 3—Comparison of catalytic activity of different materials. Conditions: Cracking reaction temperature, 380±5°C; catalyst loading, 10% (w/v); product end point, 250°C.
product end point of 250°C. At 11 wt% catalyst loading [10% (w/v)], the conversions of the feed to lighter products were obtained as 35.6%, 58.0% and 58.0%, respectively with untreated fly ash, treated fly ash and commercial zeolite as the catalysts. To determine the contribution of thermal cracking to the conversion, reaction was carried out under otherwise identical conditions but without any catalysts and a conversion of 18% was obtained. Fig. 3 shows the conversion obtained at different times with different materials as catalyst. It is evident from this figure that the treated fly ash is superior to commercial zeolite at almost all conversion levels.

Conclusion

Catalytic cracking is an important refinery operation. All modern refineries are equipped with fluid catalytic cracking unit that uses costly zeolite catalysts. Attempt was made here to develop cracking catalyst from low-cost raw material.

Fly ash from a Thermal Power Plant was treated hydrothermally with the treated material having the similar structure as the zeolite. The performance of this material as a cracking catalyst was investigated with a heavy oil fraction as the cracking feedstock. The catalyst was found to perform equally well as commercial zeolite.

The outcome of the study is promising in further development of a technology for the utilization of waste coal ash which is an unwelcome by-product inevitably formed through human activities using coal as a raw material for energy source. Thus, the present result is useful in opening the way for disposal of industrial solid waste products to control the pollution for environmental protection.

References