

Separation and Utilization of Value-Added Products from Combustion Fly Ash

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INTRODUCTION

The utilization of power-plant-derived fly ash has an impact on the cost of power production from coal. The usage has been hindered by recent shifts to low NO_x burners which can increase the carbon content of the ash above the specification (ASTM) for its use in cement applications. Due to the drastic changes in the carbon content in the fly ash, post-combustion beneficiation has been a recent focus of research. Beneficiation processes can generate a valuable unburned organic product and inorganic fly ash product, and these two constituents can be collected and used as commercial products. The unburned organic fraction can be recycled back to the burner as a fuel or used as a catalyst, activated carbon, or catalyst support. The purified inorganic fraction can be utilized as a cement additive or the material for synthesizing molecular sieves. Improved beneficiation and utilization schemes for fly ash can transform it from a waste material, with associated disposal costs, to a valuable product.

Researchers at National Energy Technology Center (NETL) over the last several years have developed a dry triboelectrostatic separation technology for the removal of mineral impurities from pulverized coal and fly ash [1]. In addition, NETL's researchers have extended the agglomeration method utilized for coal beneficiation for the recovery of unburned carbon from fly ash [2]. These techniques have recently been applied to the separation of carbon from fly ash to yield an ash rich product that meet specifications for use in cement applications as well as carbon rich products for other novel applications. The focus of current research is to take the resulting separated fractions, from both dry triboelectrostatic and wet agglomeration processes developed by NETL to explore their potential applications (i.e., activated carbon, molecular sieves, catalytic application, and catalyst supports).

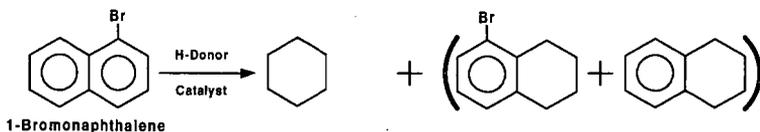
One possible application for fly ash is the synthesis of zeolite products: a process analogous to the formation of natural zeolites from volcanic deposits [3]. Both volcanic ash and fly ash are fine-grained and contain a large amount of aluminosilicate. Amorphous aluminosilicates are the major mineral compounds present in Class F fly ash along with other crystalline minerals, including quartz, mullite, hematite, lime, and feldspars. These chemical and mineralogical features make fly ash a good candidate for zeolite synthesis. In natural conditions, these volcanic deposits may be converted into zeolites by the influence of percolating hot groundwater. This process may take tens to thousands of years under natural conditions. Acceleration of this natural process could result in a cost effective, large scale industrial application for fly ash. Within laboratory conditions, this conversion can be expedited to days. The goal of current research is to establish the optimal conditions for the formation of zeolite products from fly ash.

Carbon materials have been used for a long time in heterogeneous catalysis, because they can act as direct catalysts or, more importantly they can satisfy most of the desirable properties required for a suitable support [4]. Among many types of carbon-supported catalysts (graphite, carbon black, activated carbon, etc.), high surface area activated carbon and carbon black are the carbon materials of choice for most carbon-supported catalysts. Thus, novel applications of carbon derived from fly ash are the focus of current research. Carbon as a catalyst support for the NO_x reduction reaction and carbon as a catalyst for dehalogenation applications are examined.

Farcasiu et al., [5] reported the catalytic activity of carbon black in selective dehydroxylation and dehalogenation reactions under reductive conditions in the presence of a hydrogen donor. Their work has shown that carbon black can catalyze dehydroxylation and dehalogenation reactions of aromatic compounds only in the presence of a hydrogen donor. Within this study, the catalytic reactivity of the carbon concentrates derived from fly ash was examined for hydrodehalogenation of 1-Bromo naphthalene reactions.

EXPERIMENTAL

The details of the dry triboelectrostatic separators and wet agglomeration column were described elsewhere [1,2]. Fly ash (carbon content of 7.74 wt.%) derived from the combustion of a Black Creek Pittsburgh seam coal was utilized for the preparation of carbon concentrates. The 2 wt. % Rh on carbon catalysts were prepared by the impregnation of RhCl_2 over fly ash derived carbon. The NO_x reduction study was conducted in an in-situ infrared cell reactor which was reported elsewhere [6]. Three reaction temperatures, 400, 500 and 650 °C were tested for NO_x reduction activities over the Rh catalysts. The dehalogenation reactions were performed in sealed glass reaction tubes, following the previous described procedures [5]. Ratios of substituted aromatic to solvent to catalyst were 1 : 4 : 0.1. The H-donor solvent was 9,10-dihydrophenanthrene (9,10-DHP). The reaction was conducted at 350 °C for one hour and the products were identified by GC-MS and quantified by GC, using a procedure described elsewhere [5]. The zeolitization process in its simplest form is a relatively straightforward process. Fly ash from Ohio #6A and Meigs Creek coals were mixed with a hydroxide solution in a Teflon reaction vessel and incubated at ambient pressure and various temperatures. At the end of the experiment, mixtures were quenched and the reaction products recovered by filtration.



RESULTS AND DISCUSSIONS

Zeolite synthesis

An initial study using fly ash focused on synthesizing zeolites/zeolitic materials by hydrothermal activation heating. Samples of fly ash were collected by electrostatic precipitation during the combustion of Ohio #6A and Meigs Creek coals. Each sample was sieved through a 100 mesh Tyler screen and calcined at 750°C in air before being analyzed by atomic absorption spectroscopy. SiO_2 and Al_2O_3 were the major components and are the most important reagents for zeolite synthesis. Other crystalline phases identified included mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), quartz (SiO_2), hematite (Fe_2O_3), and lime (CaO).

Each fly ash was activated by NaOH and KOH solutions in a closed system. The activations were conducted using a number of Parr digestion bombs equipped with Teflon reactors. Table 1 shows the zeolite synthesis route investigated. Typically, 10.0 g of fly ash was combined with 12.0 g of alkali hydroxide and placed into a covered platinum crucible and slowly heated to 550°C in a muffle furnace. After one hour, the resultant fused fly ash/NaOH mixture was then cooled to ambient temperature and re-ground. About 6 g of fused fly ash/NaOH powder was added to 30 mL of deionized water in a closed Teflon reactor and agitated for 24 hours at room temperature. After aging the solution, the Teflon reactor was then sealed and heated to 100°C without stirring for 48 hrs. The precipitates were filtered, washed repeatedly with deionized water, and dried overnight at 105 °C.

Table 1. Zeolite Synthesis Route

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|--|
| 1. Fly Ash - 1.0 part by weight + NaOH or KOH - 1.2 part by weight |
| 2. Treated in air at 550 degrees C for 1 hour |
| 3. Ground fused fly ash to powder |
| 4. Dissolution in distilled water |
| 5. Aging of solution with stirring for 24 hours |
| 6. Heat treatment and precipitation of zeolitic material |

Physical synthesis of converted Ohio #6A and Meigs Creek fly ashes into zeolite by utilizing only the supernatant of the dissolved fused powder solutions was completed. Alternate zeolite synthesis path (Table 2) illustrates the systematic approach taken to create a higher surface area material.

Table 2. Alternate Zeolite Synthesis Route

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|--|
| 1. Fly ash 1.0 part by weight + NaOH or KOH 1.2 part by weight |
| 2. Treated in air at 550°C for 1 hour, ground to powder, fused fly ash powder |
| 3. Dissolution of fused fly ash powder in distilled water |
| 4. Separation of fused fly ash from supernatant |
| 5. Addition of aluminum hydroxide |
| 6. Aging of supernatant/aluminum hydroxide solution with stirring for 24 hours |
| 7. Heat treatment of supernatant/aluminum hydroxide solution |
| 8. Precipitation of pure zeolite material |

Fusion of NaOH (or KOH) with either the Ohio #6A or Meigs Creek fly ash prior to the aging and heat treatment steps produce high amounts of silicates and aluminosilicates, which can be easily dissolved in aqueous solutions. In utilizing the separate •Separation of Fused Fly Ash from Supernatant• step, the formation of zeolite-P is desired. A pre-determined amount of aluminum hydroxide was added after the separation of the mother liquor from the fused fly ash powder sediment. Previous studies by others have shown that Al species may be the controlling parameter in the synthesis. In comparison to the products (NaP-type zeolite) synthesized earlier, the crystalline materials obtained from this alternate synthesis path are significantly lighter in appearance (white in color), due to the absence of unreacted fly ash in solution (green in color).

The specific surface areas of the original Ohio #6A fly ash and its fused NaOH-treated counterpart produced previously were also characterized. The Ohio #6A fly ash was found to have no appreciable surface area, i.e., less than 1 m²/g. Alternatively, the NaOH-treated fly ash/zeolitic material had a specific surface area of 81 m²/g. Surface areas obtained from the KOH-treated fly ash/zeolitic and Meigs Creek samples were very similar (74 m²/g for synthesized zeolite) in comparison to the treated Ohio #6A ash. It is envisioned that the fusion of Meigs Creek ash with KOH will result in zeolite formation at lower temperatures and in less time than with NaOH. Also, the increased effectiveness of KOH should contribute largely to increasing nucleophilicity as the counter cation increases, resulting in a greater dissolution of amorphous aluminosilicates and silicates in the fused fly ash solutions.

Hydrodehalogenation

Carbon concentrates generated from NETL fly ash along with a commercial activated carbon (Black Pearl 2000) were examined for the catalytic activity in hydrodehalogenation of bromine from 1-bromonaphthalene. Five samples received from an oil agglomeration column with carbon concentrations from 37.7 % to 67.3% along with five commercial activated carbons with similar carbon concentrations by diluting with SiO₂ beads were used in the study. The results are illustrated in Figure 1. It appears that the activities of the carbon samples generated by agglomeration and the commercial activated carbon samples are comparable. The increase in carbon concentration correlates with an increase in dehalogenation activity.

NO_x reduction

The investigation of unburned carbon material as a catalyst support was conducted in collaboration with the University of Akron. NETL laboratory produced carbon samples from the fly ash derived from the combustion of a Pittsburgh bituminous coal. The University of Akron explored the catalytic properties of the carbon concentrated for NO_x reduction.

A 2 wt.% Rh on NETL carbon catalyst was prepared by impregnation of RhCl₃ over the carbon support. The Rh-Carbon catalyst was first reduced in H₂ at 400 °C then exposed to He before exposed to the reactant (1% NO in He). Three reaction temperatures 400, 500 and 650 °C were tested for NO_x reduction activities. As illustrated in Figure 2, the immediate production of N₂ (m/e:28), N₂O (m/e:44) and O₂ (m/e:16) after the introduction of NO to the reactor suggest the reactivity of the catalyst. Almost 100 % conversion of NO was observed after exposing to NO at 650 °C. Preliminary results from the University of Akron indicate that the carbon samples from

NETL do show the catalytic activities for NOx reduction.

CONCLUSIONS

Products derived from fly ash were explored for their potential applications as molecular sieves, catalytic applications, and catalyst supports. The fly ash derived zeolite with up to 75% conversion was prepared by the developed zeolite synthesis technique. X-ray diffraction analyses from the prepared zeolite are in accord with that of the natural zeolite-P. The fly ash derived carbon demonstrated good activities for hydrodehalogenation of bromine from 1-bromonaphthalene. Furthermore, the NETL carbon based Rh catalyst showed a good activity for NOx reduction.

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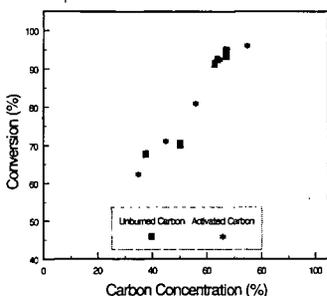


Fig. 1. The Effects of Carbon Concentrates on Dehalogenation Activities

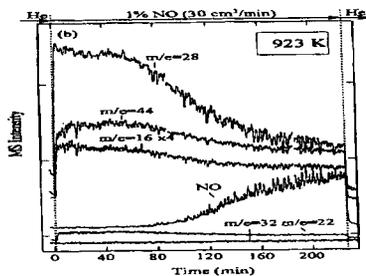


Fig. 2. The reaction of NO over Rh-Carbon catalyst