

Adsorption of SO_2 and NO_x by Zeolites Synthesized from Fly Ash, Cement Kiln Dust and Recycled Bottle Glass

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Introduction

Natural and synthetic zeolites (molecular sieves) can adsorb SO_2 and NO_x from flue gases. Unfortunately their cost (\$500-\$800 per ton on the East Coast) has deterred their use in this capacity. It has been shown however, that zeolites are relatively easy to synthesize from a variety of natural and man-made materials. The overall objective of the current work was to evaluate the feasibility of using zeolites synthesized from fly ash, cement kiln dust and other recycled materials to adsorb SO_2 and NO_x from flue gases.

Background

Zeolites occur naturally. Normally they are associated with volcanic ash deposits such as those found in Italy, Japan and the West Coast of North America. The ash forms during explosive volcanic eruptions such as the Mount St. Helens eruption a few years ago. The ash that forms during the explosion consists of very fine-grained particles of glass that are rich in alumina and silica. Because of their nature, the ash particles are very reactive. Those that deposit into alkaline lakes will slowly convert into zeolites. In the presence of water and caustic (sodium and/or potassium), the ashes react to form a wide variety of zeolites.

The synthesis of zeolites in a commercial setting is relatively straightforward. Reactive reagents are also used (sodium aluminate, sodium silicate, silica), but in this instance higher temperatures and more concentrated caustic solutions shorten the synthesis process from hundreds of years to a matter of hours or days. If one now begins to think about the potential of using industrial waste products as a source of starting materials for zeolite synthesis, one soon begins to realize that the list can contain a wide variety of materials. For example, aluminosilicate glasses with compositions similar to volcanic ash include fly ash and recycled glass cullet. If one looks for sources of caustics one can add cement kiln dust and a variety of caustic waste streams.

Synthesis procedures are straightforward: add caustic to aluminosilicate glass, allow the mixture to soak to develop precursor gel structures, and then cure at elevated temperatures ranging from 60° to 180°C. Heating the sample causes it to crystallize. The process is well documented for fly ash. More than a dozen papers are available in the literature (1-14). In addition, LaRosa et al. (15,16) and Grutzeck and Siemer (17) found that zeolites Na-P1, X and Y tended to form readily. Adding cement kiln dust (CKD) could alter bulk compositions. The high concentration of potassium in the CKD tended to reduce the need for sodium hydroxide. Recycled bottle glass provided an inexpensive source of sodium silicate (18).

Zeolites normally form on the surfaces of the fly ash particles. Once formed, the zeolites can be used for a wide variety of applications. For example some have been tested for their ability to adsorb ammonia from solution (18). It has been proposed that they be used for wastewater clean up in storm runoff impoundments and sewage treatment plants. Once loaded, they can be used as fertilizer and soil conditioner. These zeolites are also useful for adsorbing gasses such as SO_2 and NO_x from flue gases. Experiments have shown that the proposed technology is viable. Those samples cured at 150°C normally contained analcime while those synthesized at 90°C contained zeolites X, Y and NaP-1. Results suggest that SO_2 removal is 100% efficient until breakthrough and that even after breakthrough some additional adsorption takes place for a significant amount of time. Results also suggest that uptake efficiencies improve in the presence of water vapor. This is an important finding in as much as flue gas contains approximately 10-volume % water vapor. Capacity of zeolites for SO_2 ranged from 10 mg SO_2 /gram to 120 mg SO_2 /gram. These values are within the range reported in the literature for natural and synthetic zeolites.

Experimental Methods

Naturally zeolites were synthesized from fly ash with additions such as ground glass cullet and cement kiln dust. The chemistry is quite forgiving. Phases that form are determined by the bulk chemistry. Variations tend to cause different amounts of the phases to form rather than radically differing phases. The materials are mixed together in the dry state and ball milled with ceramic balls overnight. The resulting powder is then mixed with sodium hydroxide solution, allowed to soak, and then reacted at 90-180°C for a few days. Yields are on the order of 30%

zeolite. The remainder is mullite quench crystals, carbon, iron oxides and unreacted fly ash. The zeolites are filtered and rinsed on filter paper. Then they are ground and dried at 120°C.

Results

Uptake of SO₂ and NO_x was measured using a flow through test apparatus in which a synthetic flue gas containing 2000 ppm SO₂ was passed through a packed bed of various zeolites. The effluent gas was analyzed for SO₂ and NO_x using a Varian 2000 UV/VIS spectrophotometer. The adsorption of SO₂ and NO_x can be followed using their characteristic adsorption band at 284 and 380 nm. Each sample (air-dried, 120°C oven dried, or microwave dried) was tested by first recording a baseline SO₂ concentration in the stack gas by passing the stack gas through the empty adsorption unit (without the zeolite sample). Glass wool was used to seat the sample within the U-tube and so that the finely ground particles of the zeolite would not get entrained in the stack gas exiting the U-tube and entering the spectrophotometer. See Figure 1. As expected, there was little significant adsorption of SO₂ by the glass wool. Second, 1g of zeolite was weighed and placed in the U-tube between two glass wool plugs. The stack gas was passed through the sample at ~4 cc/min and the changes in adsorbance were recorded by the spectrophotometer. The procedure was repeated for each of the three types of dried samples (air dried, oven-dried at 120° C, and microwave dried). Between runs, the system was purged with N₂ gas to establish a SO₂ free baseline. The breakthrough curves were used to theoretically estimate the amount of the SO₂ removed. In as much as SO₂ content is known and total gas passed prior to breakthrough, the amount of SO₂ adsorbed can be calculated. As a check, some of the spent samples were analyzed for total sulfur content and the results obtained were compared to the theoretical calculation of SO₂ removed.

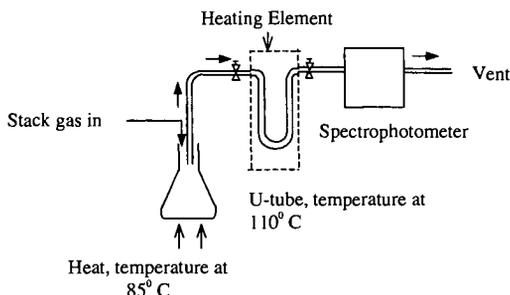


Figure 1. Details of steam generator used to mix water vapor with the simulated gas stream. Tubing running from the tanks to the glass cells was constructed of 5mm stainless steel to insure gas tightness at the ~5psi pressure needed to pass the gas through the packed bed. This set up allowed samples to be tested with or without water vapor present.

Zeolite samples that exhibited a high SO₂ capacity were also tested using the same experimental set-up with the exception that water vapor was introduced into the system. The water vapor source consisted of a 250 ml Pyrex beaker filled with a pre-weighed amount of distilled water kept at ~85°C between the flow meter and the U-tube. See Figure 1. Also, the U-tube sample holder was encased in glass wool and the temperature maintained at 110°C with heating tape to prevent any condensation of the water vapor passing through it. Once again SO₂ as ppm versus time was recorded and as a check, selected samples were chemically analyzed for their total sulfur content before and after they were tested to compare the change in sulfur content. Results are given below.

Adsorption by air-dried samples

Adsorption was first carried out in the absence of water vapor in the influent stack gas. After removing a zeolite sample from its reaction vessel, it was washed with deionized water to remove excess alkali, and then dried in room temperature air. One gram of the zeolite was weighed out and finely ground with a mortar and pestle and placed in the sample holder between plugs of glass wool. Initial tests were conducted with the background SO₂ concentration being

recorded for reference. The sample of zeolite depicted in Figure 2 showed a reasonable amount of SO_2 uptake. The break-through curve exhibited a maximum (100% SO_2) uptake for ~25 minutes.

In the next test, before introducing the sample, water vapor from the Erlenmeyer flask maintained at 85°C (Figure 1) was mixed with the gas and allowed to flow through the system. In this case, a dramatic increase in the adsorption capacity of the zeolite was seen due to the presence of water vapor. See Figure 2. Complete removal of SO_2 molecules from the influent stack gas and steam occurred for about 86 minutes after which SO_2 removal continued to occur, though 100% removal was not seen beyond that point. Sulfur analyses of the air sample tested in the presence of water vapor showed SO_2 concentrations of 10 wt% which is roughly in agreement with SO_2 uptake calculated

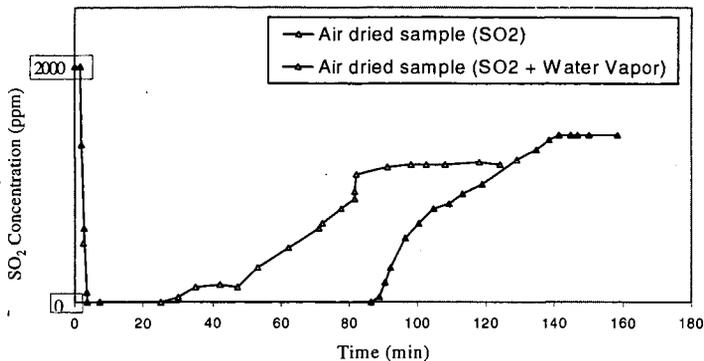


Figure 2. Breakthrough adsorption curves of air-dried zeolite sample (unknown phase) made with Class F+C fly ash, cement kiln dust and silica fume and then used to treat a simulated stack gas of (a) 2000 ppm SO_2 (~25 min to breakthrough) and (b) 2000 ppm SO_2 plus saturated water vapor (~86 min to breakthrough). Flow

from the graph in Figure 2.

Adsorption by samples dried at 120°C

Similar tests were carried out with complimentary samples that were dried at 120°C overnight. These samples (same as above) also showed an increase in adsorption in the presence of saturated water vapor. The sample showed complete adsorption in the absence of water vapor for 8 minutes but this value increased in the presence of water vapor to 23 minutes as shown in Figure 3. This again shows the increase in SO_2 uptake in the presence of water vapor. Sulfur analyses of the oven dried sample tested in the presence of water vapor showed SO_2 concentrations of 6 wt%. Surprisingly, the degree of pre-drying had a negative impact on the adsorption capacity of the zeolite.

Discussion

In the case of the air-dried samples, the dramatic increase in adsorption in the presence of water vapor is thought to occur due to the dissolution of the SO_2 molecules in the water molecules adsorbed on the surface of the zeolite sample. Subsequently, oxidation of the SO_2 molecules to sulfate and sulfite might have occurred at the temperature of 120°C , which was constantly maintained. This oxidation of SO_2 molecules is known to be temperature sensitive as previously observed by Tsuchai et al. (19) using an absorbent prepared by coal fly ash, calcium oxide and calcium sulfate. In

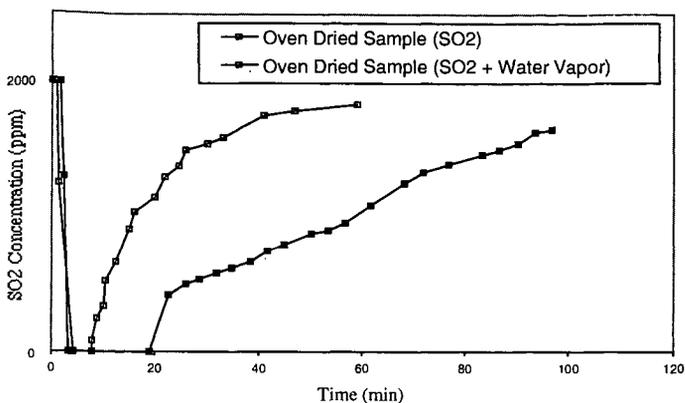


Figure 3. Breakthrough adsorption curves of same oven-dried zeolite sample with simulated stack gas of (a) 2000 ppm SO₂ (~8 min to break-through) and (b) 2000 ppm SO₂ and saturated water vapor (~23 min to breakthrough). Flow rate ~4 cc/s. Calculated uptake of 23 minute breakthrough sample=3 wt%.

this study, Tsuchai et al. proposed that a monolayer of water is formed at the surface of the absorbent in the presence of relative humidity. Above the monolayer, SO₂ dissolves in the layer while below the layer, SO₂ forms calcium sulfate due to the presence of NO and the chemical composition of the absorbent used.

In the case of the oven-dried samples, possibly, the structure of the zeolite might have undergone changes due to the overnight heating at 120°C. Though this might have occurred, an increase in adsorption was still seen in the case of the sample subjected to water vapor. This could be due to the sulfur dioxide oxidation occurring mainly at the surface of the sample rather than deep in the interior cages and channels as for the air dried sample.

Summary

A graphic representation of SO₂ adsorption results in milligrams SO₂ adsorbed per gram of tested zeolitic material is given in Figure 4. The results are typical of those obtained for air and microwave dried zeolites synthesized at 100°C. One sample (NaP-1) was regenerated by heating it in air. It was regeneratable, but less effective at adsorbing SO₂ the second time around. As seen in Figure 4, zeolites used to extract SO₂ from the simulated stack gas in the presence of water vapor could adsorb nearly 120 mg of SO₂/gram of sample. Also, surprisingly enough, zeolite samples that initially contained water (those that were air dried versus those that were dried at 110°C) tended to adsorb more SO₂ than their "drier" counterparts. Note, however, that microwave drying (MW in table) tended to increase SO₂ capacities for identical samples (oven versus microwave dried) of clinoptilolite and phillipsite run in a non-water vapor containing atmosphere. The effect of microwave drying is still being investigated, as data seem to be contradictory at this point in time.

One interesting observation was the fact that these fly ash-based zeolites were also able to adsorb NO₂ from a gas mixture containing 2000 ppm NO₂ (balance N₂). The sample in question was reacted at 90°C for 56 days. It was non-crystalline (X-ray amorphous) which is notable in as much as adsorption is usually correlated with crystallinity. Perhaps, short-range order is enough to capture certain gases. It was able to capture 88 mg NO₂/gram of zeolite. It is suggested that this property could turn out to be even more important than the zeolite's SO₂ adsorption capacity.

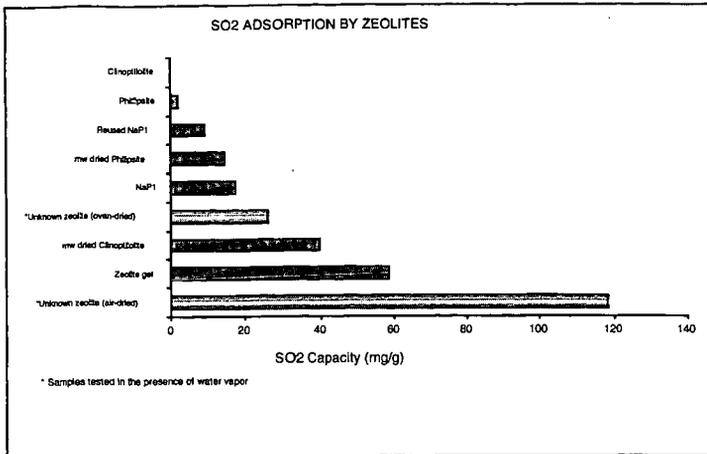


Figure 7. Relative capacities for SO₂ of samples tested with and without water vapor. Note that some of these are "dry" values and adsorption is normally two or three times higher in the presence of water vapor.

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