Some Effects of NaY Zeolite Pretreatment on Sorption Equilibria

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A zeolite (molecular sieve) will preferentially adsorb one component from a mixture even when all components have free access to the internal pore structure. We have previously published the results of studies of sorption equilibria with a wide variety of liquid binary hydrocarbon systems on NaY zeolite which had been previously activated by a pretreatment procedure commonly used in catalyst preparation, diffusion studies, or for other uses. The purpose of this study was to explore some of the effects of varying this pretreatment on sorption equilibria, specifically the effect of maximum activation temperature and the effect of presence of small amounts of water as might be adsorbed onto a previously dehydrated sieve during laboratory manipulation.

EXPERIMENT

In previous studies (Satterfield and Cheng, 1972b) the NaY was activated by driving off water or other adsorbed impurities by spreading out the zeolite in a thin layer not exceeding 3 mm in depth in a container in an oven and heating from 50° to 500°C under vacuum, increasing the temperature at a rate of 1°C/min. The zeolite was held at the final temperature for an additional several hours and then cooled to room temperature in vacuo. A thin layer is desired to prevent any self steaming of the sample. The same procedure was followed here, except that a final temperature of either 350°C or 500°C was reached. The effect of this variation in procedure on crystallinity of the zeolite was determined by X-ray diffractometry. Zeolite samples were suspended in acetate colloidal solution, placed on a glass slide, and diffractograms were obtained with a General Electric X-ray diffractometer using copper-nickel filtered radiation and 2θ angles from 40° to 4°. The degree of crystallinity was determined by comparing activated samples to unactivated samples using a summation of peak intensity correlation.

To determine the effect of moisture that might be adsorbed during laboratory manipulations zeolite samples previously activated to either 350°C or 500°C as described above were subjected to a relative humidity near 100% for 30 min. by placing a sample held in a tube in a desiccator containing water at room temperature. This substantially exceeds the exposure to moisture that one might encounter normally. In separate measurements with a thermogravimetric apparatus, zeolite powder at room temperature in contact with flowing nitrogen saturated with water vapor adsorbed water at approximately 2% of the equilibrium amount per minute.

Sorption equilibria were determined using as a model the binary system mesidine (2,4,6 trimethyl aniline)—mesitylene (1,3,5 trimethyl benzene). The separation factor as measured previously ($K = 18$) is not large, and it was expected that this system would be fairly sensitive to variation in pretreatment procedures.

Equilibrium was measured and calculated by previously described methods (Satterfield and Cheng, 1972a). For measurements on dehydrated zeolite, the binary liquid was sucked into the activated zeolite under vacuum, after cooling, and then sealed so the mixture could not be exposed to air. To determine the effect of water vapor, zeolite was placed in a tube, exposed to water vapor for 30 min. after which hydrocarbon was added and tubes were sealed.

Four combinations of pretreatment were thus studied; two temperatures of activation and completely dehydrated zeolite as opposed to zeolite exposed to water vapor. For each of the four combinations about 15 equilibrium measurements were made, at various ratios of zeolite to solution, using a binary liquid containing initially 2.5 wt. % of mesidine, the preferentially adsorbed component. More details are given by Hayhurst (1973).

RESULTS AND DISCUSSION

Values of K were found to be as follows:

Temperature of activation	Dry zeolite	Zeolite contacted with water vapor
500°C (78% crystallinity)	9.2	7.3
350°C (95% crystallinity)	17.9	13.2

The separation factor K is defined as before as $K = \dfrac{x_{a,1}/x_1}{x_{a,2}/x_2}$ where x_a and x represent the mole fraction in the adsorbed phase and the liquid phase at equilibrium and component 1 refers to the preferentially adsorbed compound, mesidine. The percent crystallinity is based on assigning 100% to the untreated zeolite.

It is seen that varying the temperature of activation can substantially affect the sorption equilibrium. The higher temperature of activation apparently led to some sintering which could affect the interaction energy with hydrocarbons. This explanation seems more likely than the development of a molecular sieving property by the sintering since both mesidine and mesitylene have the same molecular critical diameter, 8.4Å.

It is noteworthy that previous exposure to water vapor has such a minor effect on the equilibrium. Although we did not measure the amounts of water sorbed by our procedure, we presume that the zeolite cavities were substantially filled. In the previous equilibrium studies (Satterfield and Cheng, 1972) zeolite was exposed to the laboratory air for a few minutes at most, and it is believed that water pickup during this time was minor although quantitative measurements of this effect were not made. The only publication of which we are aware on effects of preadsorbed water on hydrocarbon equilibria in zeolites is a brief note by Eltekov and Khopina (1973) who report that this slightly reduced the adsorption of toluene onto NaX from solutions in *n*-heptane. The maximum effect corresponded to adsorption of about 7 water molecules per large cavity (4 m.mole/g. zeolite) and was interpreted in terms of interaction of water molecules with cation sites of different energies of interaction. The effects of preadsorbed water on sorption equilibria are of both practical and theoretical importance and deserve more detailed study.

With NaY activated to 500°C, Cheng reported a separation factor of 18 for mesidine-mesitylene, somewhat higher than the values found here. That datum was based on limited measurements and was obtained during a scouting study of a large number of binary hydrocarbon systems. Present values of K are believed to be more accurate.

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Equilibrium Data for Various Compounds between Water and Mud

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A great deal of time and money has been/is being spent in the area of water pollution control in search of an economical total recycle system for pollutants. In most of these real life situations, a specific undesirable substance has been discharged into the water for extended periods of time rendering the stream, river, etc. polluted. Once the health hazard is discovered and pollutant no longer discharged, the water is proclaimed clean and healthy. However, just because the pollutant faucet was turned off, the health state of the stream bed is not so quickly advanced as the water itself. This certainly is the case today, for example, with mercury-methy mercury effects. The purpose of this study is to evaluate the polluted stream bed by carefully studying the equilibria of various pollutants such as phenols, sulfates, and detergents between the water and soils comprising the muds, especially in the concentration range 5 to 10,000 ppm. The results from this study can be used not only to project how long it would take for a polluted stream bed to be revived but also to dramatize the total effect of water pollution to prospective polluters.

BACKGROUND

Once the flow of an undesirable pollutant is cut-off to a polluted body of water a natural period for both stream and bed reclamation is required. The water itself is cleansed much more rapidly than the bed no matter if the water is in the form of a flowing stream, river, lake, pond, etc. Therefore, the major objective of our work was to determine and consequently be able to predict the time lapse between the point at which the pollutant faucet was turned off and the point where the stream bed is healthy enough for human and animal recreation, sport, and various other uses. The term *healthy* refers to standards and specifications set by local, state, and Federal agencies for chemical and biological activity within the water. In order to evaluate this diffusion process, the degree of adsorption of pollutants in muds must first be determined. For the naturally flowing stream, the extraction of pollutants from a stream bed by rejuvenated water not only depends on local concentrations but also on the flow characteristics of the bed, that is, slope of ground rocks, bends, etc.

RELATED STUDIES

The number of articles written on the subject of water pollution has skyrocketed in the past few years. Although these articles describe current research in this area, few articles have appeared concerning a systematic method for evaluating stream bed reclamation. A most recent review of the 1969 literature published in the Water Pollution Control Federation Journal (1970) and a summary of advanced wastewater treatment processes being developed in the U.S. by Stephan and Schaffer (1970) support this statement. The studies that have been reported or funded by Federal agencies are summarized in the Water Resources Research Catalog and the Water Quality Resources Abstracts (1970). It is unfortunate that most of these studies involve the use of benthos and fishes to evaluate stream bed conditions while rarely (if at all) discussing basic chemical/engineering criteria that might be more general in nature to the overall rejuvenation process.

RESULTS AND DISCUSSION

In order to evaluate the rejuvenation of a polluted stream bed, the affinity of muds for various chemical species must be studied. This affinity is measured by contacting the pollutant species with soils in aqueous solutions until equilibrium is reached. These data are appropriately called *equilibrium* data. The first step in the collection of equilibrium data was to determine the degree of adsorption of various pollutants on muds to see if the process is purely physical or, if not, to what degree chemical interaction exists. Since the range of pollution in a typical stream might vary between high and low concentrations, two systems were chosen to cover as extended a range as possible. In the acid-mine pollution problem areas, waters are contaminated with the sulfate ion in forms such as sulfuric acid and ferric sulfate. Therefore, our initial equilibrium studies involved the sulfate system over a concentration range of 50 to 10,000 ppm by weight. Various aqueous solutions were prepared and contacted with a typical Central Pennsylvania soil until equilibrium was established. The soil consisted of particle sizes less than 0.198 mm dry-sieved with 40% less than 0.006 mm determined by