

University of Mississippi

eGrove

---

Honors Theses

Honors College (Sally McDonnell Barksdale  
Honors College)

---

2004

## Molecular Entrapments in the Nanosized Cavities of Polar-Solvated Zeolites X and Y”

Reagan Levidiotis

Follow this and additional works at: [https://egrove.olemiss.edu/hon\\_thesis](https://egrove.olemiss.edu/hon_thesis)

---

### Recommended Citation

Levidiotis, Reagan, "Molecular Entrapments in the Nanosized Cavities of Polar-Solvated Zeolites X and Y” (2004). *Honors Theses*. 2054.

[https://egrove.olemiss.edu/hon\\_thesis/2054](https://egrove.olemiss.edu/hon_thesis/2054)

This Undergraduate Thesis is brought to you for free and open access by the Honors College (Sally McDonnell Barksdale Honors College) at eGrove. It has been accepted for inclusion in Honors Theses by an authorized administrator of eGrove. For more information, please contact [egrove@olemiss.edu](mailto:egrove@olemiss.edu).

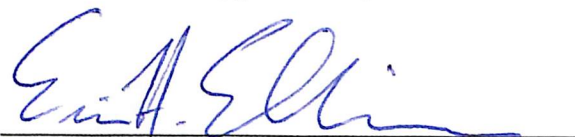
ENTRAPMENT OF POLYNUCLEAR AROMATIC HYDROCARBONS IN THE  
POLAR-SOLVATED ZEOLITES X AND Y

by  
Reagan Levidiotis

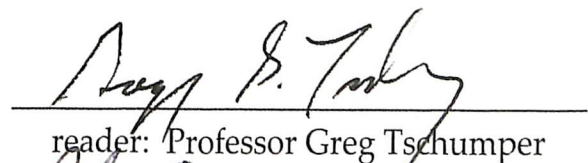
A thesis submitted to the faculty of The University of Mississippi in partial  
fulfillment of the requirements of the Sally McDonnell-Barksdale Honors College

Oxford  
May 2004

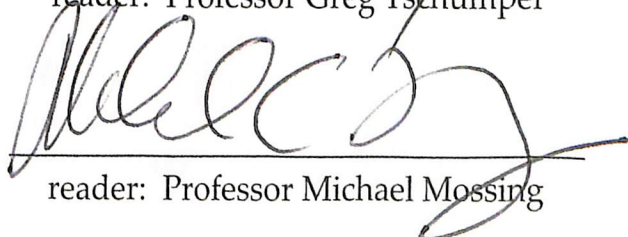
Approved by



advisor: Professor Eric Ellison



reader: Professor Greg Tschumper



reader: Professor Michael Mossing

© 2004  
Reagan Levidiotis  
ALL RIGHTS RESERVED

## ABSTRACT:

Zeolites are microporous aluminosilicates that are used in many capacities as media for ion – exchange, catalysis, and molecular sieving. The internal structure of zeolites consists of silica and alumina tetrahedra arranged in such a way to form two types of cages: sodalite cages and supercages. Polynuclear aromatic hydrocarbons (PAH's) such as pyrene can get into the supercages by means of adsorption from a nonpolar solvent, but cannot be extracted from the supercage by submersion of the zeolite in a polar solvent. In this study the zeolites X and Y (which are synthetic analogs of the naturally occurring zeolite faujacite) were used to observe this effect for a variety of PAH's and to determine under what conditions, if any, PAH's can be removed from zeolites. The results indicate that pyrene and other PAH's are indeed trapped within the supercages of the zeolites and that heating and evacuating the zeolite discs prior to exposure to a polar solvent makes the effect even more obvious. It was also observed that zeolite X retains a higher percentage of PAH's than does the Y form; that the PAH does not become a derivative species while in the zeolite; and that some cages trap molecules while others do not. We conclude from this study that higher ionic content in the zeolite cages caused more PAH to be retained and also caused "trapping cages." Heating and evacuating the zeolite discs caused an increase in molecular movement within the zeolite, which allowed PAH molecules to find trapping sites deep within the zeolite. This phenomenon permitted PAH's that were located on the exterior of the zeolite to become trapped in cages not normally filled by probe. A possible application of this study could be as a separation technique for molecules of different sizes.

## TABLE OF CONTENTS

LIST OF FIGURES.....	v
LIST OF TABLES.....	vi
INTRODUCTION.....	1
EXPERIMENTAL.....	6
RESULTS.....	11
DISCUSSION.....	19
CONCLUSION.....	24
REFERENCES.....	25

## LIST OF FIGURES

Figure 1	Formation and Grouping of Sodalite Cages to Form Different Zeolites.....	3
Figure 2	Supercage in Zeolite Y.....	4
Figure 3	Schematic of Disc Preparation and Heating/Evacuating Set-up.....	8
Figure 4	Comparison of Supercage Opening Aperture (7.4 Å) and Probes Used...12	
Figure 5	Graph of Rate of Anthracene Extraction Out of Zeolite X.....	17
Figure 6	Schematic of zeolite particle and trapping cages within the particle.....	21

## LIST OF TABLES

Table 1	Percent Probe Remaining in Zeolite Following an 18-hour Extraction in Methanol.....	13
Table 2	Comparison of Zeolite X and Y Powders and Discs.....	14
Table 3	Loading Concentrations and Percent Retention for Pyrene.....	15
Table 4	Pyrene Retention Percentages: Pre-treatment vs. No Pre-Treatment....	17

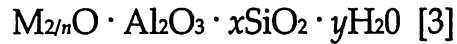
## INTRODUCTION:

Zeolites are microporous, crystalline aluminosilicates that are widely used as media for ion-exchange, catalysis, and molecular sieving. As ion-exchange media, some zeolites are highly selective, and can be used to isolate and concentrate certain cations. [1] As catalysts, zeolites have been used for oil refining and petrochemical transformations and for the synthesis of fine and specialty chemicals. Their usefulness as catalysts originates from both their high surface area and adsorption capacity, and from the fact that the sizes of their cavities are in the range for many molecules of interest (5 Å to 12 Å.) [2] Zeolites can also be used as molecular sieves, which means they act as probes of molecular size. To be used as a molecular sieve, the structure of the zeolite must remain intact after complete dehydration. [3] Zeolites are materials of great diversity, and although many applications have already been found, new uses of these materials continue to be pursued.

The framework of zeolites consists of aluminum, silicon, and oxygen in the form of silica and alumina tetrahedra. These tetrahedra are arranged in such a way that no two aluminum atoms share the same oxygen atom. [4]



Zeolites can be represented by the empirical formula:



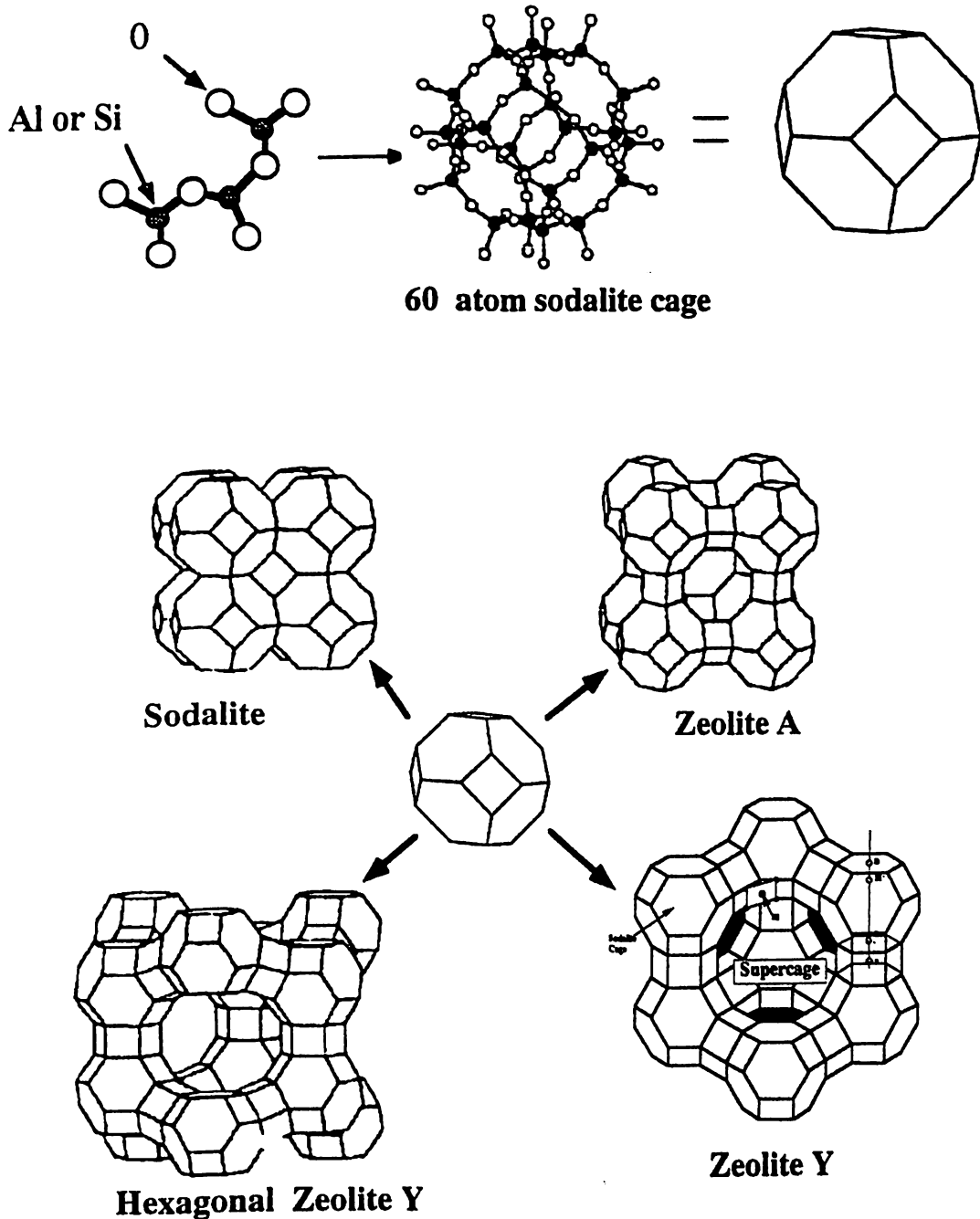
where M is a cation of valence  $n$  (typically sodium, calcium, or magnesium.) [5]

It is the substitution of aluminum for silicon in the tetrahedral framework that gives the negative charge, and exchangeable cations exist in the pores of the zeolite to balance out the negative charges. The cations are located at various positions in zeolites determined by X-ray crystallography. The most common cations are Group I and Group II elements, and they can generally be exchanged by conventional methods. [5]

The zeolite used in this research, faujacite, is a naturally occurring mineral that comes in two forms – zeolite X and zeolite Y, which are synthetic analogs. The difference between the two forms is the ratio of silicon to aluminum. (Zeolite X has a Si/Al ratio less than 2.0, while zeolite Y has a ratio of Si/Al greater than 2.0. The higher aluminum character gives the X form higher negative charge.) The silica/alumina tetrahedra are arranged in such a way as to form “cages.” The smaller cages are called sodalite cages, which are arranged to form a larger supercage. [Figure 1]

The aperture of the sodalite cage is approximately 2.2 Å and will generally allow only water (or a smaller molecule) inside it; oxygen is too large to enter into a sodalite cage. The supercages are much larger, with a pore opening of

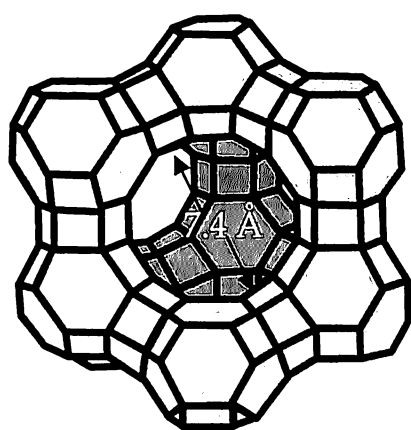
Figure 1: Formation and Grouping of Sodalite Cages to Form Different Zeolites. [6]



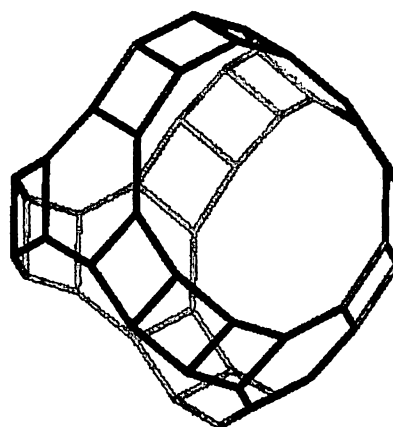
7.4 Å and an interior diameter of 13 Å. The supercages can hold a maximum of 28 H<sub>2</sub>O molecules compared to a maximum of only 4 H<sub>2</sub>O molecules in the sodalite cage. The fact that supercages have smaller opening aperture diameters

than actual interior diameter [Figure 2] leads to interesting effects, such as the fact that certain molecules can get into the openings and move freely within the supercage.

Figure 2: Supercage in Zeolite Y. A) Supercage opening aperture measures 7.4 Å, while its interior diameter is 13 Å. [3] B) Table comparing sodalite cage properties with supercage properties.



A.



supercage framework

B.

	<u>Sodalite cage</u>	<u>Supercage</u>
Aperture	2.2 Å	7.4 Å
Diameter	6.6 Å	13 Å
Volume	151 Å <sup>3</sup>	822 Å <sup>3</sup>
H <sub>2</sub> O max.	4	28

Of specific interest in our research is that polynuclear aromatic hydrocarbons (PAH's) are able to get into the cages but remained "trapped" within the zeolite when the zeolite is bathed in a polar solvent such as methanol.

This phenomenon can be observed using PAH's such as pyrene and anthracene, which were placed in the internal cavities of the zeolites X and Y by adsorption from non-polar solvents. When the loading solvent was removed by evacuation and the sample was subsequently bathed in a polar solvent, it was determined that a significant fraction of the PAH remained in the zeolite pores. By contrast, experiments have shown that PAH's can be completely extracted from the pores of silica gel when submerged in polar solvents. The reason for this effect is that the polar solvent competes for polar adsorption sites (SiOH groups) on the silica surface. The phenomenon of the trapped PAH molecules in polar-solvated zeolites X and Y prompted further testing and experimentation.

## EXPERIMENTAL:

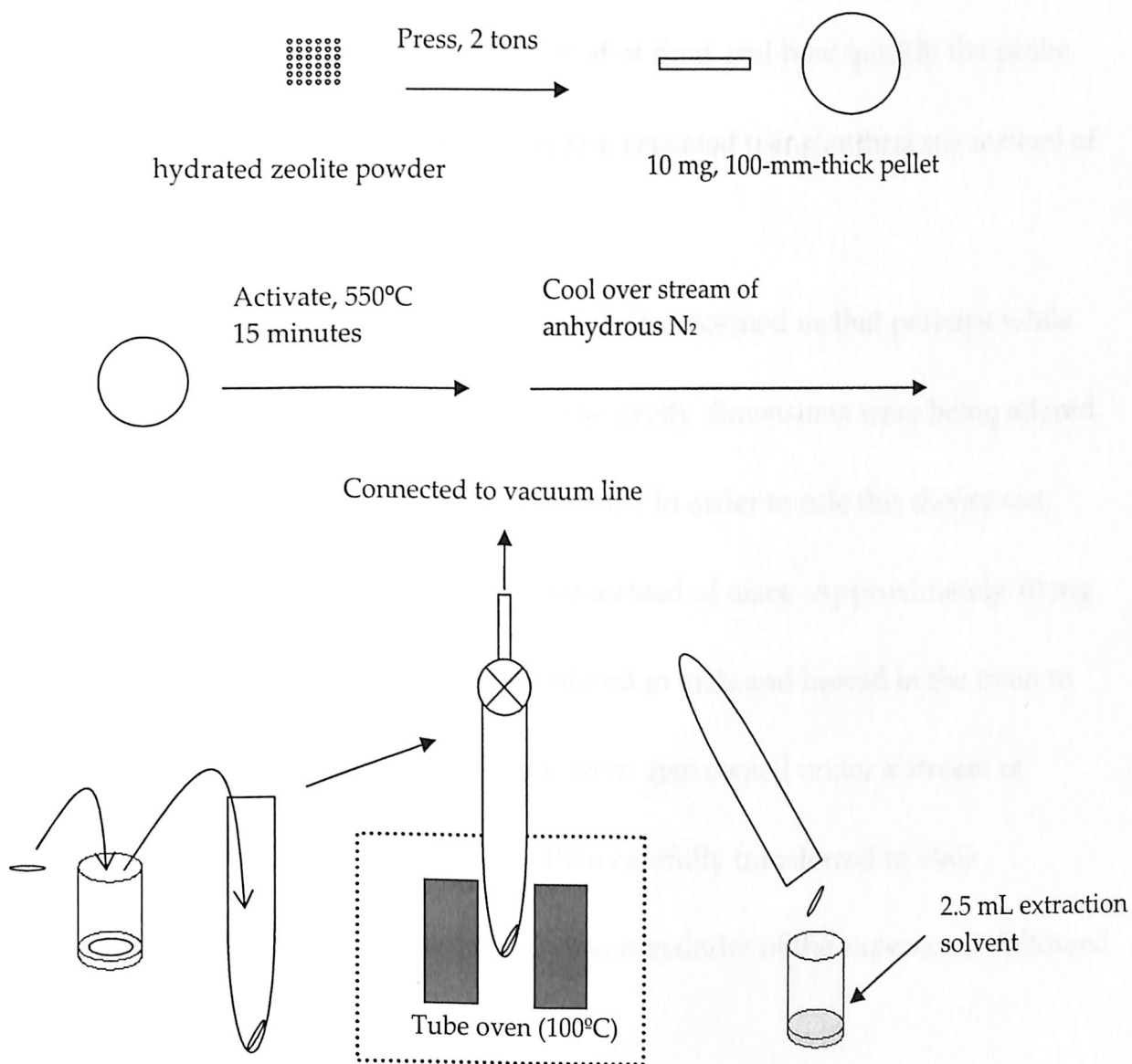
Disc Preparation: The test media for our experiments were self-supported discs, which were pressed from hydrated zeolite powder. This procedure was performed by putting a small amount of zeolite powder into a die cell and compressing the cell at two tons with a lab press. Each disc, approximately 10 mg, 13 mm wide, and 100  $\mu\text{m}$  thick, was then dehydrated by heating in an oven at 550°C for 30 minutes. This procedure ensured that each disc was as dry as possible and that the weight of water did not contribute to the weight of the disc. Next, each disc was cooled over a stream of dried  $\text{N}_2$  gas (to avoid air hitting the zeolite discs and rehydrating) and placed in a solution of PAH in cyclohexane. Discs were made from both zeolite X and zeolite Y powders, and for each test performed, a disc of each form was used. The chemical composition of the sodium exchanged forms are given as follows: Sodium X,  $\text{Na}_{80}\text{Al}_{80}\text{Si}_{112}\text{O}_{384}$ , (Si/Al: 1.4); and Sodium Y,  $\text{Na}_{55}\text{Al}_{55}\text{Si}_{137}\text{O}_{384}$ , (Si/Al: 2.5). [7]

Standard Procedure: Pyrene and other probes were loaded onto the cooled zeolite discs by adsorption from solutions of the probe in 2.5 mL cyclohexane. Cyclohexane was used as the loading solvent because it is non-polar; polar solvents cannot be used for this purpose as there would be

competition for adsorption sites by the solvent. The vial was then placed on an orbital shaker and agitated for 2 hours, so that the pyrene had proper time to evenly adsorb to the zeolite disc. The number of molecules loaded onto the disc was determined using quantitative absorption spectroscopy, where the depletion in concentration of the loading solution was measured by the use of standard curves. The disc was removed and evacuated for 10 minutes at 100°C to remove the loading solution. [Figure 3] The heated, dried disc was then removed from the vial and placed in 2.5 mL of either methanol, tetrahydrofuran (THF), or acetonitrile, which were used as the extraction solvents. Each extraction solvent was stored over dried type 3A molecular sieves to remove any water that was potentially in the solvent. The disc remained in the extraction solvent overnight (approximately 18 hours.) The following morning, the extraction solvent was removed from the vial, and the absorbance of the solution was measured using an Ocean Optics UV/visible CCD array spectrophotometer. Standard curves were made with known concentrations of pyrene, and the absorbance was graphed versus concentration. (This yielded a straight line,  $y = mx + b$ .) The absorbance measurement was determined from the spectrophotometer, and the standard curves could be used to interpolate the concentrations from the measured absorbance. The concentration that was measured in cyclohexane indicated how much was loaded initially. The measured concentration in

Figure 3: Schematic of Disc Preparation and Heating/Evacuating Set-up.

The zeolite powder was compressed to a flat 10 mg disc and heated. Pyrene (and later, other PAH's) were loaded onto the zeolite disc from the loading solvent and heated in a tube oven while being connected to a vacuum line for 10 minutes. Finally, the disc was transferred to a vial with 2.5 mL extraction solvent.



methanol (representative of how much was extracted) was subtracted from this value and the result indicated how much pyrene had been retained on the disc.

Kinetic studies: Pyrene was adsorbed onto discs by using the standard procedure. The disc was then transferred to methanol. The methanol was extracted and observed spectroscopically after five, ten, twenty, forty, and eighty minutes, and two, four, six, and finally eighteen hours to determine how much remained on the disc after a certain period of time, and how quickly the probe came off the disc. This procedure was also repeated using anthracene instead of pyrene.

Zeolite powder versus zeolite discs: It concerned us that perhaps while pressing the zeolite powder into discs, the cavity dimensions were being altered, and thus causing the trapping phenomenon. In order to rule this theory out, tests were performed using free powder instead of discs. Approximately 10 mg of both forms of zeolite powder were placed in vials and heated in the oven to remove water from the samples. They were then cooled under a stream of nitrogen gas. The dried powder was then carefully transferred to vials containing 2.5 mL of pyrene solution. The remainder of the experiment followed the standard procedure.

Derivative Test: Another concern was that perhaps while being trapped in the zeolite cages, a reaction was occurring between the pyrene and the zeolite that changed the chemical structure of pyrene and formed a derivative species. We therefore examined whether or not the entrapped molecules were in fact the



original species loaded on the zeolite. This experiment was carried out by use of samples which had been previously subjected to an overnight extraction at room temperature. These samples were then thoroughly rinsed and placed in 10 mL of fresh solvent in a sealed, Teflon-lined, hydrothermal reaction bomb. The extraction was allowed to proceed for three days at 125°C. The solvent was removed from the bomb and a spectrometer was used to determine the absorption spectrum.

## RESULTS:

It was obvious from fluorescence studies that pyrene had been entrapped within the zeolites; UV excitation of pyrene in sodium X or sodium Y bathed in methanol produced bright fluorescence. Our initial interests with this phenomenon was to quantitatively determine how much pyrene was retained within the zeolites. The other intention of our research was to observe the behavior of pyrene and other PAH's smaller than pyrene in dehydrated zeolites X and Y and to examine whether smaller specimens can also be trapped in the zeolite. Prior to our studies, we used silica gel in place of the zeolite discs as a control to show that it is possible to completely remove pyrene from silica gel. Indeed, all adsorbed pyrene came off the silica gel when submerged in a polar solvent. Silica is a mesoporous material, which means that the pore dimensions are greater than 2 nm and much larger than that of zeolites. The silica used in our study had a pore diameter of 6 nm. (Zeolites, which are microporous materials, have diameters less than 2.0 nm.) [2] Our research interest with the zeolites X and Y was to further explore the nature of the "trapped" PAH molecules and to learn under what conditions molecules are more likely to

be a factor in accounting for any differences in percent retention among the zeolites. The observed difference in retention, most notably for anthracene, may be related to the higher ionic content of zeolite X. Also, it is important to mention that the phenomenon of molecular entrapment in faujacite was not unique to pyrene. Anthracene, perylene, and 9,10 - dimethylanthracene were retained to a certain extent as well. These PAH's were tested following the same procedure that was used for pyrene. Although all of the PAH's tested did remain to a certain extent within the zeolites, retention rates were generally higher for pyrene, perylene and 9,10 – dimethylanthracene than for anthracene. Most likely, this is due to the smaller dimensional width of anthracene versus the other probes, compared to the zeolite aperture of 7.4 Å.

Table 1: Percent Probe Remaining in Zeolite Following an 18-hour Extraction in Methanol. The initial probe loading (#/supercage) is given in parenthesis.

Zeolite:	Perylene, (0.01)	9,10 – dimethylanthracene, (0.01)	Anthracene, (0.006)	Pyrene, (0.008)
Zeolite X	98%	97%	68%	97%
Zeolite Y	99%	91%	21%	68%

The tests that were done to compare the powdered form of the zeolite versus the disc indicate that, for the same zeolite under the same treatments, approximately the same amount of pyrene is retained. [Table 2] Thus, pressing the samples does not damage the zeolite pore structure such that it prevents the

PAH from leaving the disc, and sample architecture (powders vs. self-supported discs) can be ruled out as the reason that the PAH's are retained. Self-supported discs, however, are much easier to work with than powders, because they are more convenient to transfer and handle. Once we established that the sample architecture was not the reason that pyrene was trapped, discs were used for the remainder of our experiments.

Zeolite/Form	Percent retained
Zeolite X (powder)	97%
Zeolite X (disc)	97%
Zeolite Y (powder)	68%
Zeolite Y (disc)	74%

Table 2: Comparison of Zeolite X and Y Powders and Discs. Probe loadings were 0.008/supercage.

Our test using the reaction bomb indicated that the original species remained in the zeolite. The reaction bomb enabled us to achieve a higher temperature for extraction by increasing the temperature of the solvent (in the reaction bomb the pressure is able to increase to greater than 1 atm, and thus changes the boiling point.) By increasing the temperature, it was possible to extract a fraction of the molecules that were held by the zeolite at room temperature. For pyrene, the fluorescence and absorption spectrum of the bomb supernatant solutions was indicative of the original species. For pyrene it was possible to observe changes in III/I vibronic bands of the fluorescence spectrum that typically coincide with changes in solvent polarity, [8] by evaporating the

extraction solvent and redissolving the pyrene in cyclohexane. For derivatized or substituted pyrene, it is not possible to observe the dramatic changes in the vibronic bands typical for pyrene. [8] This discovery reemphasizes the fact that, at room temperature, one compound can go in but the same compound cannot come out.

The extraction solvent can also be ruled out as a cause for entrapment of pyrene. This phenomenon is not unique to methanol; when THF or acetonitrile was used as an extraction solvent, pyrene was still retained in virtually the same amounts as methanol. This discovery nullified the hypothesis that pyrene entrapment was unique to methanol.

The loading concentration of the pyrene did not change how much pyrene was retained on the disc. [Table 3] When ten times as much pyrene was used in

Table 3: Loading Concentrations and Percent Retention for Pyrene.

Zeolite species	Percent retained
Zeolite X , loaded 0.008/supercage	95%
Zeolite Y, loaded 0.008/supercage	68%
Zeolite X, loaded 0.08/supercage	96%
Zeolite Y, loaded 0.08/supercage	79%

the loading solution, the percentage retained in the discs was similar to the results when less probe was used. These results indicate that retention is not due to how much pyrene is initially loaded onto the disc, and there is not simply a very small number of what can be considered trapping cages. Many of these cages must exist in order to notice the effect.

Another effect we observed was how sample handling affected the results. Table 4 shows that the discs that were heated with evacuation had a higher retention of pyrene than discs that had not been evacuated and heated prior to placement in methanol. The evacuation dried the discs further, which prevented any water from getting on the disc and occupying any sites in the disc for pyrene to locate, and the heating sped up movement of the PAH's. The bigger difference in  $Y$  can be attributed to the fact that within the zeolite, the PAH molecules are located on the exterior particle surface. The heating and evacuating caused the pyrene molecules to go deeper into the cavities of the zeolite, where they would not otherwise go, and this phenomenon resulted in a significantly higher retention in the  $Y$  form.

The rate of extraction of anthracene and pyrene from the zeolite disc was monitored at intervals over an 18 hour period, and it appears that the rates of extraction depend on both probe size and ionic content.

Zeolite, Loading concentration	Immediate transfer from cyclohexane to extraction solvent	Heating/evacuation pre- treatment
Zeolite X, 0.008/supercage	78%	97%
Zeolite Y, 0.008/supercage	23%	68%

Table 4: Pyrene Retention Percentages: Pre-Treatment versus No Pre-Treatment. Both X and Y forms resulted in higher retention with pre-treatment, but the effect is more drastic for Y.

Figure 5 illustrates the rate of extraction of anthracene from zeolite X over an 18 hour period. Anthracene in sodium X leaked out much more slowly over the 18 hour period than it did out of sodium Y. We attribute this fact to the high ionic character of sodium X.

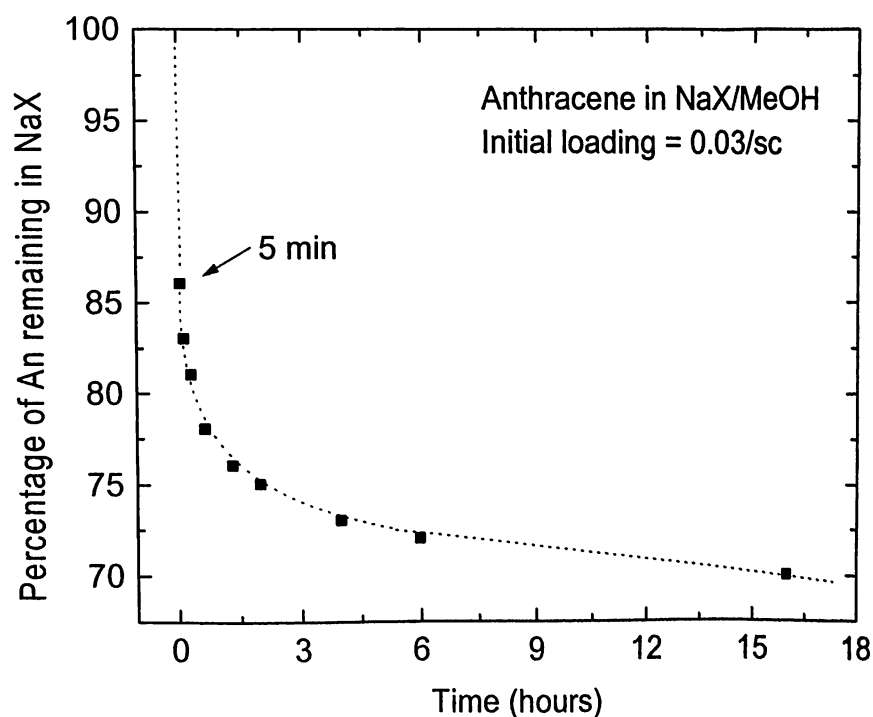


Figure 5: Graph of Rate of Anthracene Extraction out of Zeolite X.

Similarly, pyrene also came out of sodium Y at a slower rate than anthracene. This fact is due to pyrene's larger dimensions, and so more time is required for it to diffuse completely. Pyrene did not come out of sodium X at a rate that could even be measured. This makes sense as the size of the molecule and the amount of ion-ion interactions would not permit much pyrene to leave the disc at all. Our results show that for anthracene, when put in a sodium Y zeolite disc, the molecules speed out at a more rapid rate; any anthracene that comes out of sodium Y does so within five minutes. This fact is due to the fact that anthracene is such a small molecule relative to pyrene, and the Y form of faujacite has fewer ion interactions that would prevent the molecule from coming out. The fact that some molecules leave the discs immediately while some remain on the zeolite for an indeterminate amount of time indicates that some cages are more likely to be "trapping" cages than others. Anthracene molecules in the "non-trapping" cages can simply diffuse out, which is affected by the ionic content of the zeolite. Removal from trapping cages seems to be a more highly activated process and large molecules such as pyrene remain for long periods of time in these cages. (Discs that were loaded with pyrene nine months prior to the completion of this paper still exhibit fluorescence.) It is not obvious why some cages contain more ions than others do, however.



## DISCUSSION:

Our research with zeolites X and Y show that unlike silica materials, which can have polynuclear aromatic hydrocarbon probes removed from their pores by use of polar solvents, this method cannot be used to completely extract PAH's from within the zeolite. In porous silica materials, polar solvents block adsorption sites and solubilize the PAH according to bulk solvent effects. Our work with zeolites shows that this clearly does not happen in the micropores of zeolites. The trapping effect in zeolites can be described as a type of nanoscale phenomenon, in which bulk solvent behavior cannot be assumed.

It was observed that higher concentrations of the probes were retained in zeolites X than in the Y form. By definition, zeolite X has a lower Si/Al ratio than does the Y form, which means more ions are present in the X form. We attribute the observation of higher probe retention to the fact that zeolite X has more ionic content and thus more ion interactions than does the Y form, which would prevent a large amount of PAH from desorbing from the disc. We can conclude from this result that probe retainment increases with ionic content of the zeolite.

Pyrene is not the only PAH that cannot be extracted from the zeolites with polar solvents. Perylene and 9,10-dimethylanthracene were also retained within

the zeolites. Even anthracene, a smaller molecule, was retained, although in much lower percentages than pyrene, perylene, and 9,10 – dimethylanthracene. Pyrene, perylene, and 9,10 – dimethylanthracene are bigger probes which means that they would have less entropic freedom once in the supercage. Their dimensions are similar, which is the most probable cause of them having a higher percentage of probe retained within the zeolite. Their dimensions are very close to the entry aperture of the supercage so they are a tight fit in getting into and out of the zeolite.

The experiment using the reaction bomb further supported the fact that the PAH molecules could go into the zeolite but could not come out. The molecules were not changed in the experiment (or once they entered the supercages) to form larger chemical structures that could not exit the zeolites. Because we could confirm that the species in the zeolites were not larger derivatives of the original molecules, we could rule out chemical derivatization as the cause of entrapment.

Regardless of what polar extraction solvent was used to remove the pyrene, the percent of pyrene retained on the zeolite remained fairly constant. This fact remained true no matter how much probe was loaded onto the zeolite; more molecules do not indicate that more cages will trap them. The values also did not change when the powdered form of the zeolite was used. From these

results, we can conclude that sample architecture, extraction solvents, and loading concentrations can all be ruled out as causes for entrapment.

The theory for the high percentage retention when heating/evacuating pre-treatment were used is that because the heating increases molecular movement, it thus increases the likelihood of pyrene finding and adsorbing to a trapping cage, especially if the trapping cage is not located on the outside of the disc. When pyrene was adsorbed to the zeolite by use of nonpolar solvent, the pyrene was retained in trapping cages that were located superficially (near the exterior of the particle surface, not deeper into the particle.) Other pyrene molecules that were not retained in the supercages were held weakly to the outside of the zeolite. [Figure 6]

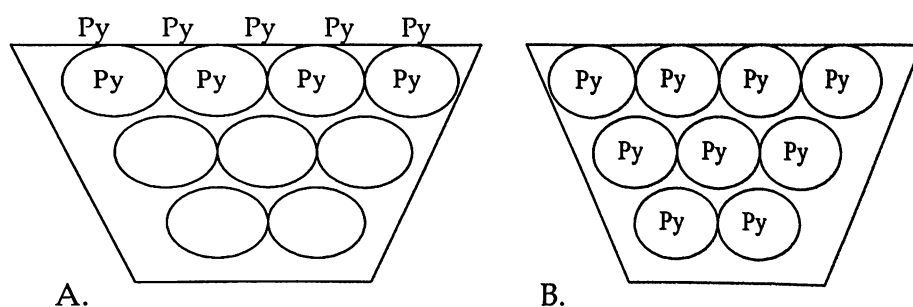


Figure 6: Schematic of zeolite particle and trapping cages within the particle. A) Without heating and evacuating the discs, pyrenes are trapped in the supercages located near the external surface of the zeolite. Other pyrene molecules are held to the outside of the particle by weak interactions which are easily overcome by submerging the disc in a polar solvent. B) Heating and evacuating the zeolite disc prior to submersion in polar solvent causes an increase in molecular movement which allows any pyrene that is on the outside of the disc to enter the disc and find trapping molecules that are deeper in the zeolite particle.

Without heating and evacuating, this pyrene would be rinsed off the disc once submerged in methanol or other polar solvent, while the pyrene in the trapping cages would be retained. When the discs were heated and evacuated, however, the molecules of pyrene sitting on the surface of the zeolite were allowed to move deeper into the zeolite particle, occupying trapping cages that would not normally be occupied.

Finally, the results from the kinetic studies/rates of extraction indicate non-uniformity among the cages within the discs – that some supercages trap molecules while others do not. The kinetics study with anthracene indicated that there is a relationship between trapping cages and ionic content. Because anthracene was able to come out of zeolite Y so quickly, but came out at a much slower rate in zeolite X, we can assume that the trapping cages have higher ionic content and that the ions appear to block transport. This assumption would mean that almost all of the supercages in zeolite X were trapping cages. In addition to the ionic content of the zeolite, an additional factor that contributes to the rate at which molecules leave the non-trapping cages would be the size of the probe.

The results obtained from these experiments were informative about the trapping nature of the zeolites X and Y, but also raised some questions as well. One question that could promote further study is could other methods (besides

polar solvation) be used to remove probe molecules from microporous materials.

Another question that was raised is if the trapping effect could be used as a

separation technique to separate two different molecules. Further

experimentation could yield answers to these questions.

## CONCLUSION:

- The kinetics study indicates an inhomogeneity among the discs and that the cages are not equivalent. Some are more retentive (i.e., the "trapping" cages), while others are more willing to let molecules escape.
- At least for pyrene, the extraction solvent used does not matter – the PAH is retained to a similar extent in methanol, acetonitrile, and THF.
- Heating increases molecular movement and increases the chance of molecules finding a trapping cage.
- Pyrene remains pyrene. The final result is the original species and not a derivative.
- Zeolite X retains more molecules than does the Y form. This is attributed to increased ionic content which means more trapping cages.
- Theory of entrapment: once a PAH molecule diffuses into a supercage, it will remain trapped there if the supercage is in an area of high ionic content within the zeolite.

## REFERENCES:

1. Barrer, R.M., *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*. Academic Press: London, 1978.
2. Corma, Avelino, *From Microporous to Mesoporous Molecular Sieve Materials and Their Use in Catalysis*. Chem. Rev. 1997, 97, 2373 – 2419.
3. Breck, Donald W., *Zeolite Molecular Sieves: Structure, Chemistry, and Use*. John Wiley and Sons: New York, 1974.
4. Ramamurthy, V., and Caspar, J. V., *Photophysical Studies of Organic Molecules Included Within Zeolites*. Mol. Cryst. Liq. Cryst., 1992, 211, 211 – 226.
5. Ramamurthy, V., *Photochemical and Photophysical Studies within Zeolites*. Chimia, 1992, 46, 359 – 376.
6. Stucky, G. *Nanochemistry and Nanoclusters: The Beginning of Matter*. Naval Research Reviews, 1991, 44, 28 – 39.
7. Ellison, Eric H. *Influence of Oxygen on the UV – Photocatalyzed Generation of Pyrene Cation Radicals in the Zeolites X and Y*. J. Phys. Chem., 2004, 108, 4607 – 4618.
8. Kalyanasundaram, K., and Thomas, J. K., *Environmental Effects on Vironic Band Intensities in Pyrene Monomer Fluorescence and Their Application in Studies of Micellar Systems*. Journal of the American Chemical Society, 1977, 99, 2039 – 2044.