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Intrazeolite Photochemistry. 15. Influence of Aging, Inert Gases, and Water on the Mobility of Pyrene Molecules on the Faujasite NaY

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The mobility and location of pyrene within the cavities of the faujasite NaY have been examined using fluorescence and diffuse reflectance techniques. The photophysical properties of pyrene within the zeolite framework show that upon incorporation the pyrene molecules are initially distributed in the outer cavities of the zeolite granules. This leads to a high number of doubly occupied cavities and large excimer emission; this emission shows only 20−25 ps delay, suggesting that excimer-forming molecules are required to undergo only small intracavity motions. With time (days) the distribution of pyrene within the cavities of the zeolite equilibrates and monomer emission dominates the spectra. The time required for this equilibration to take place is shown to be highly dependent on sample preparation. In particular, water and hexane hinder pyrene redistribution, while this process is faster under nitrogen than in samples under vacuum. The detection of delayed fluorescence on the microsecond time scale on freshly prepared samples indicates that there is movement of the pyrene molecules located on the external surface of the zeolite after sample preparation; no delayed fluorescence is observed after 1−2 days.

Introduction

Pyrene has been a favorite photochemical probe for studies in many heterogeneous systems, including zeolites.[1−9] Zeolites are crystalline aluminosilicates whose three-dimensional structures provides a restricted environment for organic probe molecules. The supercages in faujasites have a formal diameter of ∼13 Å and are connected to four neighboring cages through four windows of about 7.4 Å in diameter.[10,11] These supercages are large enough to accommodate up to two pyrene molecules.[5] Pyrene is well-known to form an excimer with distinct fluorescence centered around 480 nm, which is significantly red shifted from the ∼400 nm monomer fluorescence.[12] Comparative studies of excimer and monomer emission can yield information on local probe concentration and mobility.[5,9,13−16]

Despite several reported studies on pyrene in zeolites,[6−9,13−19] particularly faujasites, we feel that some fundamental questions remain unanswered. In particular, questions relating to the incorporation protocol, aging of the sample, and presence or absence of an "inert" atmosphere deserve more attention than they have thus far received. It has been generally assumed that the pyrene−zeolite complex has reached a stationary state where no relocation−redistribution of pyrene is taking place; our results suggest that in some situations this is not a good assumption. To illustrate this point, Figure 1 represents a selection of spectra;[20] the details of data acquisition and overall trends will be discussed in full in the Results and Discussion. For the moment, suffice to say that the sample of Figure 1 has approximately 10% average occupancy level for the cavities, leading to an expectation of ∼1% double occupancy.[21] Yet, the emission spectrum on the day of sample preparation is dominated by excimer emission, while 31 days later monomer emission dominates the signals. This sample was sealed in a quartz tube under nitrogen; at 15 days the spectrum shows more

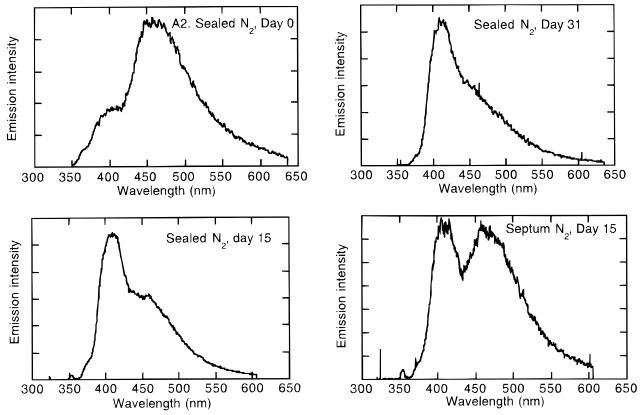

Figure 1. Emission spectra of pyrene−NaY complex obtained upon 355 nm excitation. Spectra are of sample A1 (sealed with septum and purged with N_2 prior to photolysis) 15 days after sample preparation and sample A2 (sealed quartz tube under N_2) 0, 15, and 31 days after sample preparation.

excimer than after 31 days, but it is clear that the excimer-to-monomer evolution is already largely complete. In contrast, a "twin" sample that was capped with a rubber septum (but flushed with fresh nitrogen before recording each spectrum) shows almost equal monomer and excimer emission after 15 days. Thus, despite the fact that these samples were prepared in an identical manner and both were apparently exposed exclusively to a nitrogen environment, significant differences in the mobility of the pyrene monomers were observed. The difference between these two samples (Figure 1, bottom) is that the septum-sealed sample must have absorbed some water, which restricts pyrene mobility.[5,16] Clearly, the "day-0" sample was not in equilibrium; further, the conditions of preparation and storage also affect the evolution toward equilibrium.

In the present work, we have used fluorescence spectroscopy and time-resolved diffuse reflectance techniques to study the effect of various parameters relating to the preparation of zeolite−pyrene complexes on the ability of pyrene to move

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within the cavities and the channels of zeolites. Time-resolved diffuse reflectance techniques allow the monitoring of triplet behavior in the microsecond time scale. These results are compared with those obtained by monitoring the delayed fluorescence of pyrene in the same time scale. Our study is based on the well-known photophysical properties of pyrene and provides unique information on the aggregation, microenvironment polarity, and mobility of the guest.

Experimental Section

Sample Preparation. The zeolite LZ-Y52 molecular sieve (NaY zeolite, Si/Al = 2.6) used in this study was obtained from Aldrich. Pyrene (Aldrich, 99% purity) was recrystallized from ethanol prior to use. Hexane (BDH, OmniSolv) was dried with anhydrous magnesium sulfate (American Chemicals Ltd.).

NaY zeolite (3.2 g) was baked at 550 °C overnight (16−20 h) to activate the zeolite by removal of the absorbed water. After activation the zeolite was taken from the oven and quickly transferred to a dry nitrogen environment (glovebag). The activated zeolite was allowed to cool and was then added to a solution of 0.445 g of pyrene dissolved in 100 mL of dry hexane. The mixture was magnetically stirred for 1 h, centrifuged, and decanted. The zeolite was resuspended in 30 mL of fresh hexane and stirred for another 0.5 h. The supernatant was removed after centrifuging the sample and added to the first aliquot.

The wet zeolite−pyrene composite was placed into a vacuum desiccator (ca. 0.1 Torr) and connected to a vacuum line. The vacuum was applied for 6 min, and then the desiccator was filled back with dry nitrogen. This procedure removed all visible traces of hexane from the sample. The zeolite−pyrene complex was then transferred back into the glovebag to ensure that no water was reabsorbed into the zeolite framework. The pyrene−zeolite complex was then split into three batches. One batch was further divided and placed into individual quartz laser cells (3×7 mm^2 Suprasil quartz). The treatment of individual cells included either (1) capping with a septum and purging with nitrogen, (2) sealing under nitrogen, (3) vacuuming out at room temperature and sealing under vacuum, or (4) vacuuming out at liquid nitrogen temperature and sealing under vacuum. The sealing of the quartz tubes ensured that the samples did not reabsorb any water during the course of these long experiments. After preparation, the samples were stored in the dark at room temperature. The two remaining batches of the pyrene zeolite complex were returned to the vacuum desiccator and vacuumed out under reduced pressure for a total of 1 or 3 h. After the vacuum had been removed, the samples were placed into quartz cells and sealed according to the procedures described above. For the sample where the vacuum was applied for 3 h two samples were sealed under vacuum at room temperature. One sample was sealed under 0.1 Torr and the other sample under 0.3 Torr.

In another series of experiments, a sample of the wet zeolite−pyrene composite was dried under vacuum in a desiccator for 6 min and then divided into individual laser cells. One of the samples was sealed with a septum and purged with nitrogen. The remaining four samples were placed directly on the vacuum line and sealed after pumping for 15 min, 1 h, 2 h, and 4.5 h. The vacuum was monitored and was kept constant at ~0.06 Torr.

Samples in sealed cells were then used in the laser experiments without further modification. Cells capped with a septum were repurged with dry nitrogen for at least 30 min prior to photolysis. For the oxygen-quenching studies, samples in cells capped with a septum were flushed with oxygen prior to photolysis. As a precaution, the sample was shaken after each laser shot in order to maximize the exposure of a fresh surface to the laser beam.

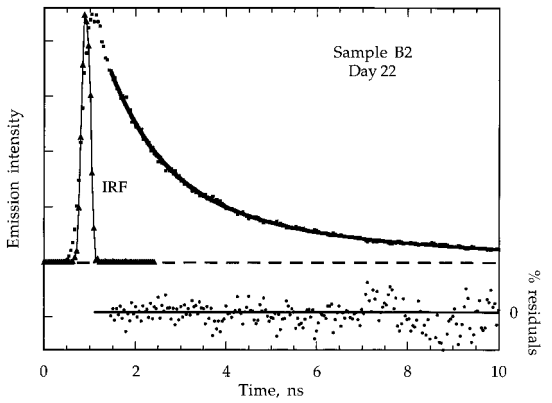


Figure 2. Monomer fluorescence from sample B2 on day 22 and instrument response function. The data have been deconvoluted and fitted to a double-exponential function. The distribution of residuals is shown at the bottom of this figure.

The amount of pyrene incorporated into the sample was determined by the amount of pyrene remaining in the combined hexane solutions after the incorporation procedure was complete. The concentration was determined using UV−vis spectroscopy and a calibration plot. In both samples the loading level was about 0.1 pyrene molecules/cavity.

Fluorescence Measurements. Our experimental setup for time-resolved fluorescence consists of a Hamamatsu C4334 streakscope coupled with a spectrograph as the detection system and a Continuum picosecond PY-61-10 Nd:YAG laser equipped with an external amplifier as the excitation source. The timing of the laser pulse striking the sample and the acquisition of data is accomplished using a 130 ns optical delay unit and a delay box. The 35 ps 1064 nm light pulse from the YAG laser was first directed through an external amplifier and then into an optical delay unit (Hamamatsu White Cell) using a series of dichroic mirrors. After exiting the optical delay path the 1064 nm light was directed through second and third harmonic generators in order to generate 355 nm light to be used as excitation source. The 355 nm light (35 ps pulses; 0.25 mJ/pulse) was then concentrated on the sample cell using front-face excitation. The resulting emission was collected with a series of lenses and focused into a spectrograph and into the Hamamatsu streak camera described above. The time resolution of the system depends upon the streak camera settings, but for very short time scans it is limited by the 35 ps laser pulse, as the streak camera has a time resolution of <15 ps. For long time scales, such as the 20 ns on which Figure 2 is based (only 10 ns displayed), the instrument response function (IRF) has a half-width of approximately 180 ps. Kinetic data were then fitted with a monoexponential or biexponential function either with the Hamamatsu software provided with the streakscope or with similar analysis packages from other suppliers. Figure 2 shows a representative biexponential fit and the corresponding distribution of residuals. There is little doubt that a higher level multiexponential analysis or fits to a distribution of rate constants could provide a better fit to the experimental data; for the purposes of our semiquantitative analysis, a biexponential fit proved adequate.

The data were then viewed on a video terminal and transferred to a Macintosh Quadra 650 computer for storage and analysis. Operation of the streak camera and data analysis was run using PhotoLumi Software supplied with the Hamamatsu instrument.

For the delayed emission studies where longer time scales were needed the attenuated third harmonic pulses (355 nm, 10

TABLE 1: Sealing Procedure Employed for the Samples

	vacuum desiccator pretreatment		
	6 min	1 h	3 h
N_2/septa	A1	B1	C1
N_2/quartz seal	A2	B2	C2
room-temp vacuum quartz sealed	A3	B3	C3, C3*[a]
77 K vacuum quartz sealed	A4	B4	C4

[a] Sample C3 sealed at 0.1 Torr; sample C3* sealed at 0.3 Torr.

ns pulses, 1 mJ/pulse) from a Surelite Nd:YAG laser were employed. The timing between the excitation source at the sample cell and the triggering of the Hamamatsu C4334 streak camera was accomplished using a delay unit (Stanford DG353). The streak camera was triggered 1 μs after laser excitation of the sample. In this way the prompt emission was completely gated out, and the high gain settings required for low-intensity delayed emission measurements could be employed.

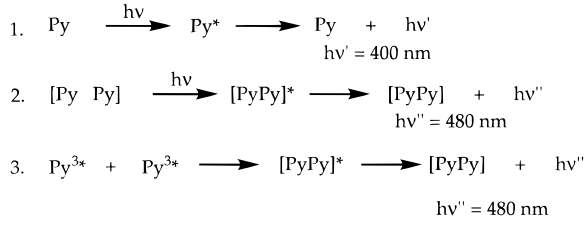
Time-Resolved Diffuse Reflectance. The experimental setup for time-resolved diffuse reflectance was similar to that previously described.[22] A Tektronix 2440 digitizer was used to capture the signals from the monochromator−photomultiplier system. The data acquisition, handling and storage was accomplished with a PowerMacintosh computer and software written in the LabVIEW 3.1.1 environment from National Instruments. The third harmonic (355 nm, ≤10 ns pulses, ≤20 mJ/pulse) from a Surelite Nd:YAG laser was used for sample excitation.

Results and Discussion

In preliminary studies of pyrene incorporated onto NaY zeolite, the samples were "sealed" with a rubber septum under a nitrogen atmosphere. It was noted that after a few days or weeks, the emission spectrum from these samples had changed, normally with an increase in monomer fluorescence at the expense of excimer emission. The effect was not due to oxygen contamination, since the nitrogen atmosphere was always reintroduced prior to the measurements. The question arising from this preliminary observation was whether the effects resulted exclusively from some form of pyrene redistribution (aging) over extended periods of time, or whether the absorption of adventitious water[16] had either caused or assisted the changes. Examination of the literature on pyrene emission from solid heterogeneous systems shows that while the incorporation and measurement protocol are frequently well defined, changes that accompany the aging of samples over extended periods have not been the subject of significant studies. We note that the occupancy levels (and therefore initial excimer contribution) in the present work are usually higher than those employed in earlier literature work.[8,14,16] It is possible for the loading of the samples to have some effect on the redistribution kinetics studied here. These possible loading effects are not explored in this contribution.

A set of 12 samples was prepared based on a single incorporation of pyrene as described in the Experimental Section. The sealing procedure and label identifying each of the 12 samples are given in Table 1. In general, samples sealed after room-temperature vacuum pumping were sealed at pressures between 0.1 and 0.3 Torr. In the specific case of sample C3, we purposely sealed two samples at slightly different pressures. No difference in their emission spectra or time evolution was observed, indicating that the changes discussed below cannot be due to differences in the conditions under which the samples were sealed. Measurements referred to as "day 0" were carried out within 5 h following preparation. Samples were stored under normal laboratory conditions, but protected from light.

SCHEME 1



The dimensions of pyrene, approximately 7.2 Å × 13 Å, ensure a relatively tight fit in the cavity of NaY, which normally contains four sodium counterions. Up to two pyrene molecules can fit in the cavity. Interestingly, it is probably this tight fit through the window that is responsible for the long relocation times observed here. Small molecules can migrate quite readily,[23] while molecules that cannot fit through the window can be incorporated only by *ship-in-a-bottle* synthesis and are essentially incarcerated.[24−26]

Emission from the pyrene system can arise from three distinct origins, as illustrated in Scheme 1. We anticipate that excimer emission will occur only when two molecules share the same cavity at the time of excitation (eq 2) with the exception of long-lived delayed excimer fluorescence eq (3), discussed separately. Literature data on diffusion coefficients[23] and our own results (vide infra) suggest that intercavity hopping of pyrene does not take place in the nanosecond−picosecond time scale. Reactions 2 and 3 in Scheme 1 have been written as producing *only* excimer. In principle, it is possible for some of these events to lead to monomer also; however, we feel it is unlikely for two pyrene molecules to share a supercage and *not* form the excimer.

The data acquired in our system provides simultaneous spectral and kinetic information, and it is possible to extract either emission spectra at different times following excitation or time profiles at any wavelength or wavelength range. Out of necessity the data presented in this article were selected to illustrate central points. A more extensive (even if still partial) set is included as supporting information. We systematically found excimer emission (monitored at ∼480 nm) to be significantly longer lived than monomer emission (monitored at 400 nm). This is illustrated in Figure 3.

Picosecond Phenomena. An attempt was made to establish if excimer formation was a delayed process;[27,28] i.e., if the time required for the encounter between an excited- and a ground-state pyrene could be determined. Figure 4 shows that the growth of both the monomer and excimer emissions is virtually instantaneous. However, taking the monomer emission as a reference, a small but reproducible delay of approximately 20−25 ps is observed in the excimer emission. This slight delay suggests that the excimers may result from double occupancy of the supercages but that some intracavity reaccommodation/realignment of the two pyrenes is required for excimer formation. Note that the traces of Figure 4 were recorded in a fresh sample (C3* sample, day 0).

Fluorescence Emission in the Nanosecond Time Scale. These emissions were recorded using a 35 ps laser pulse at 355 nm for excitation. Unless otherwise indicated, spectral data were obtained by integrating over 20 ns, starting immediately after laser excitation. Typically, the signal from 600 pulses over 60 s were accumulated for our measurements. If for any reason the data had to be obtained again, a fresh surface was exposed when the experiment was repeated. Figures 5−8 show the

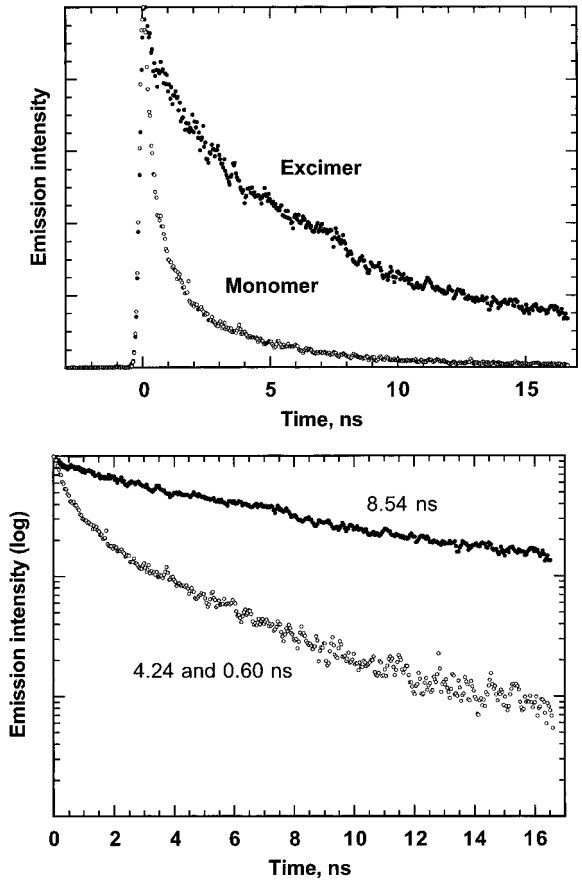


Figure 3. Fluorescence decay profiles (top) of pyrene−NaY complex obtained upon 355 nm excitation of sample Al (sealed with septum and purged with N_2 prior to photolysis) 9 days after sample preparation. The monomer emission was monitored at 400 nm (a) and excimer emission was monitored at monitored at 480 nm (b). The log plot (bottom) leads to biexponential (monomer) and monoexponential (excimer) decays.

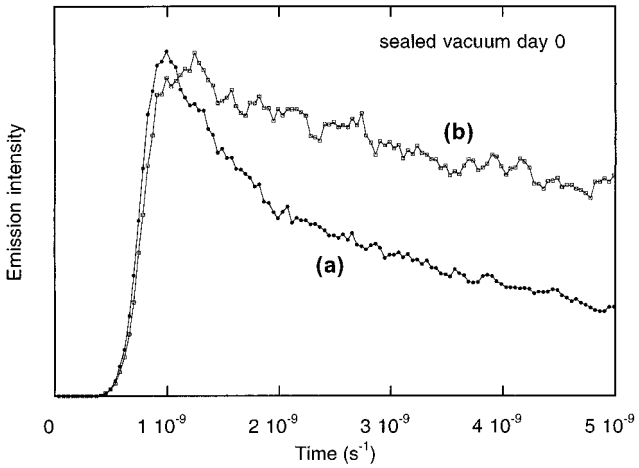


Figure 4. Fluorescence decay profiles on short time scale of monomer (a) and excimer (b) emission obtained upon 355 nm picosecond excitation of sample C3* (sealed quartz tube under vacuum at room temperature) 0 days after sample preparation.

spectra obtained 0, 9, 15, and 31 days after inclusion for samples sealed under nitrogen with a rubber septa or a quartz seal, as well as samples sealed under vacuum, with the vacuum applied at either room temperature or 77 K. All these samples were pretreated under vacuum in a desiccator for 6 min. The effect of different pretreatment is discussed later.

Examination of Figures 5−8 reveals several trends: all samples have comparable excimer-to-monomer intensity ratios

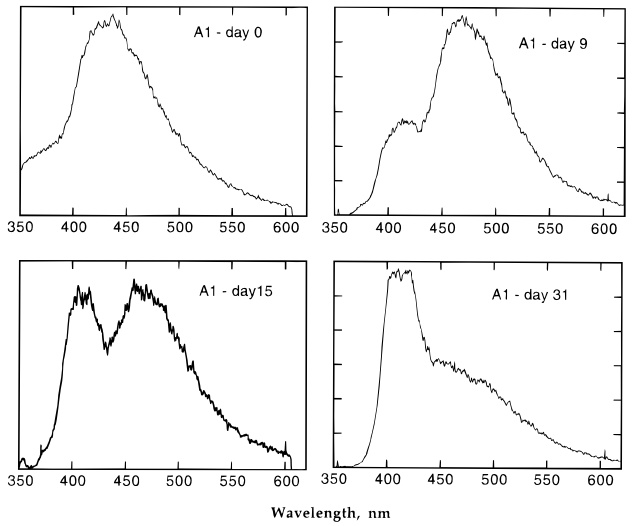


Figure 5. Emission spectra of pyrene−NaY complex obtained upon 355 nm excitation. Spectra are of sample A1 (sealed with septum and purged with N_2 prior to photolysis) 0, 9, 15, and 31 days after sample preparation.

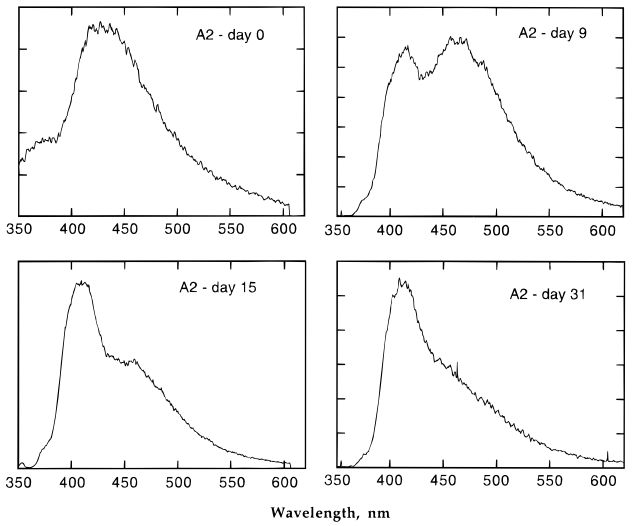


Figure 6. Emission spectra of pyrene−NaY complex obtained upon 355 nm excitation. Spectra are of sample A2 (sealed quartz tube under N_2) 0, 9, 15, and 31 days after sample preparation.

on day 0, with the excimer emission being much greater than monomer emission. This ratio is clearly higher than that expected from a statistical distribution of pyrenes, which in our case corresponds to ca. 1% double occupancy. In all cases aging of the samples for 1 month results in the observation of essentially only monomer emission. In other words, emission from all samples is very similar on day 0 and after 1 month; we anticipate that small differences in the excimer-to-monomer emission ratios after 1 month of aging will also eventually disappear if one waits sufficiently long. Monomer fluorescence reveals a small shift as the spectral evolution progresses. At this point it is unclear if this is a true shift or a reflection of changes in the underlying vibrational structure as the sample ages.

While all samples exhibit similar emission characteristics at day 0 and at day 31, significant differences are observed on the dynamics of this evolution. In particular, the sample sealed with a rubber septum shows a distinctly slower evolution toward the monomer-only situation. We believe that this reflects the absorption of water into the zeolite, which is known to restrict probe mobility. In addition, to our surprise, we find that the samples under vacuum show a slower evolution than those

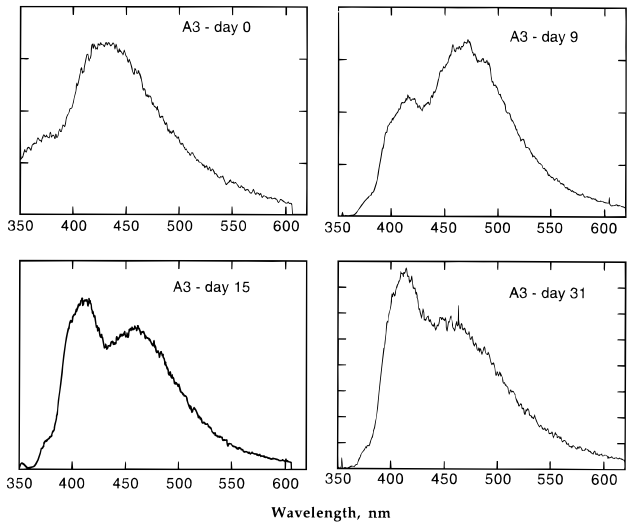


Figure 7. Emission spectra of pyrene−NaY complex obtained upon 355 nm excitation. Spectra are of sample A3 (sealed quartz tube under vacuum at room temperature) 0, 9, 15, and 31 days after sample preparation.

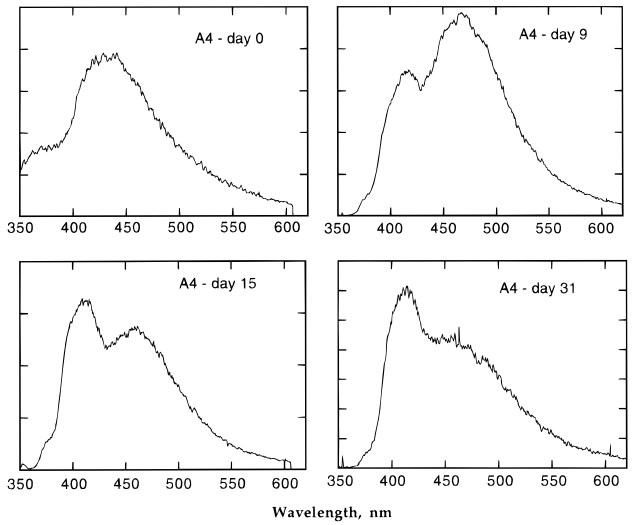


Figure 8. Emission spectra of pyrene−NaY complex obtained upon 355 nm excitation. Spectra are of sample A4 (sealed quartz tube under vacuum at 77 K) 0, 9, 15, and 31 days after sample preparation.

sealed under nitrogen. This is not due to loss of material during application of vacuum, since no differences are seen between samples evacuated at room temperature or at 77 K. We would not anticipate any loss of material at 77 K. Thus, the presence of gaseous nitrogen appears to enhance pyrene mobility, just as if nitrogen was a "lubricant" within the zeolite environment.

The "lubricant" properties of nitrogen, while unexpected, can probably be rationalized on the basis of association with active sites. While this may be weak and rather modest in the case of nitrogen at room temperature, it may be rapid enough to provide an increased opportunity for pyrene to migrate to one of the neighboring cavities.

Figure 9 shows the effect of longer vacuum desiccator pretreatment as monitored after 9 days for a sample sealed under vacuum at room temperature. Clearly, the fact that excimer emission is almost absent in the sample evacuated for 3 h but distinctly detectable in the sample evacuated for 1 h indicates that the longer pretreatment facilitates the evolution toward the monomer situation; i.e., the sample ages faster the longer the pretreatment. We believe this observation can be explained on the basis of the removal of molecules that can hinder pyrene mobility during the pretreatment. In principle, the molecule

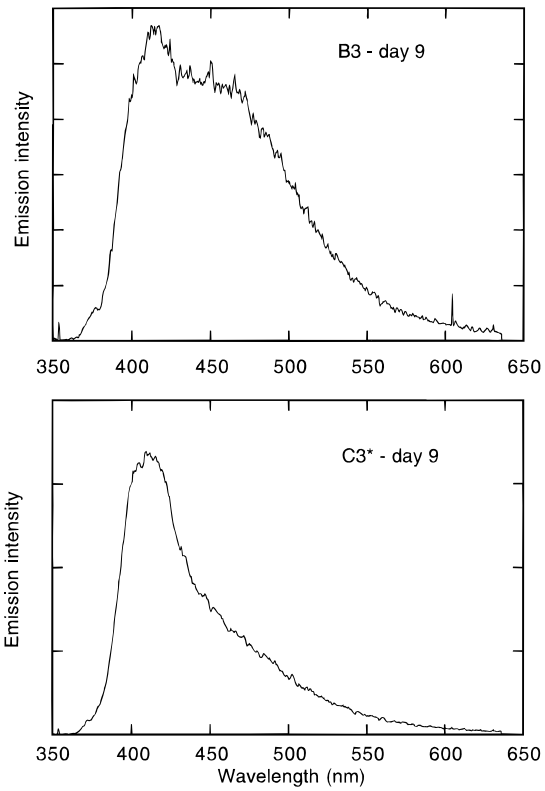


Figure 9. Emission spectra of pyrene−NaY complex obtained upon 355 nm excitation. Spectra are of sample B3 (sealed quartz tube under vacuum at room temperature after 1 h vacuum) and sample C3* (sealed quartz tube under vacuum at room temperature after 3 h vacuum) 9 days after sample preparation.

removed can be absorbed water or residual hexane (used as inclusion solvent). We feel that removal of hexane is a more likely explanation, since up to this point in the protocol for sample preparation the zeolite has had virtually no exposure to ambient moisture following the activation/drying at 550 °C.

The decay of the pyrene monomer and excimer fluorescence showed distinct kinetic behavior. The excimer emission was found to follow clean monoexponential kinetics. In contrast, under no experimental conditions did the decay of the pyrene monomer follow simple monoexponential behavior. The monomer emission followed a more complex pattern which could be adequately fit by double-exponential analysis. Figure 10 (see also Figure 2) shows the decay traces for sample B3 at 0, 9, and 31 days. For example, after 9 days, the monomer emission follows approximately biexponential decay with lifetimes of 0.70 and 5.78 ns, while the excimer decays monoexponentially with a lifetime of 9.09 ns. As already pointed out, excimer emission is systematically longer than the monomer emission, a situation that contrasts with that found in homogeneous solution where the excimer is usually shorter lived than the monomer.[29,30]

A more extensive set of lifetime values has been included with the supporting information. We note that in some cases the data exclude either monomer (fresh samples) or excimer (aged samples) lifetimes, simply because for some samples a given type of fluorescence may be too weak for reliable/significant measurements to be carried out.

The monomer lifetimes reported here are significantly shorter than those reported in earlier publications discussing pyrene emission in the same or other zeolites.[5,13,16] Several factors may have contributed to these differences: First, our occupancies are significantly higher than those in earlier reports. The relatively high loading was required to promote double occupancy in fresh samples and to facilitate the aging studies

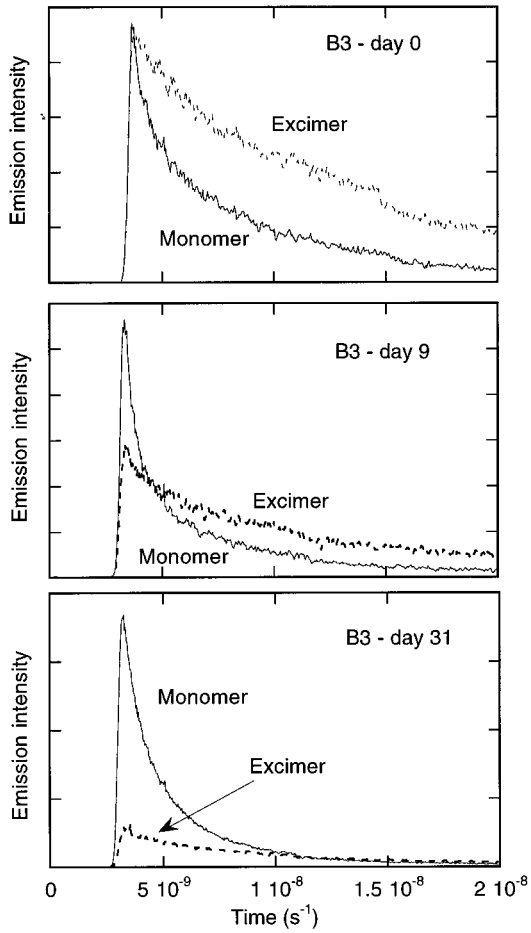


Figure 10. Fluorescence decay profiles of pyrene−NaY complex monitored at 400 nm (monomer emission, solid line) and 480 nm (excimer emission, dashed line) obtained upon 355 nm excitation of sample B3 (sealed quartz tube under vacuum at room temperature after 1 h vacuum). Kinetics were taken on day 0, 9, and 31 after sample preparation.

conducted by us. In addition, at 10% occupancy level, once random occupancy is established, a pyrene molecule occupying a cavity by itself has an approximately 40% probability that another pyrene molecule will occupy one of the four neighboring cavities. Recent work from our group has demonstrated that rapid interaction with neighboring molecules (nearest-neighbor cavities) is not uncommon.[31,32] Even those molecules that have reached single occupancy must have pyrene-occupied nearest-neighbor supercages, since the initial evolution from double to single occupancy can involve only interconnected cavities. Second, the very dry zeolite samples may have provided a highly polar environment that typically tends to shorten the lifetime of singlet excited pyrene. Finally, earlier literature work has generally employed nanosecond detection and nanosecond excitation sources. The short fluorescence component observed by us is easier to detect with picosecond laser sources and picosecond detection capabilities. While the lifetimes observed can be detected with nanosecond deconvolution techniques, their observation and analysis are undoubtedly easier with the methods employed here. Independently of the actual values, the short lifetimes are consistent with a highly polar environment, since this is a well-known dependence for pyrene fluorescence, although effects of this magnitude are unprecedented in solution.

Another set of samples was prepared in which the pyrene−zeolite composites were exposed to vacuum (0.06 Torr) for various periods of time before being sealed. The pretreatment

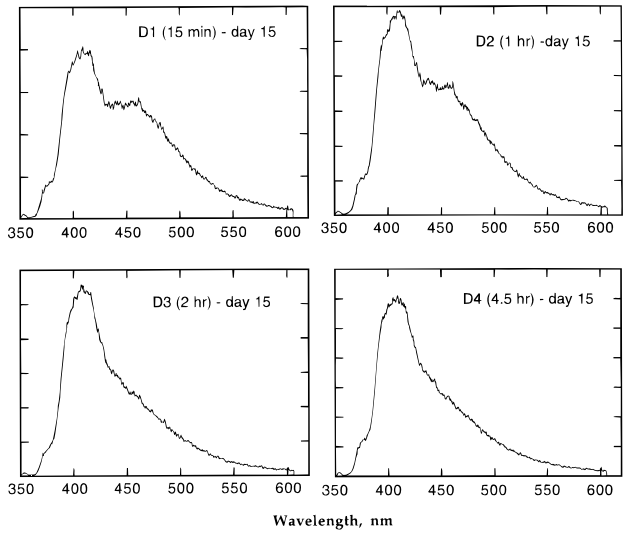


Figure 11. Emission spectra of pyrene−NaY complex obtained upon 355 nm excitation. Spectra are of samples (sealed in a quartz tube under vacuum at room temperature) D1 (after 15 min vacuum), sample D2 (after 1 h vacuum), sample D3 (after 2 h vacuum), sample D4 (after 4.5 h vacuum) 15 days after sample preparation.

in all those samples consisted of 6 min of drying in a vacuum desiccator. Samples D1, D2, D3, and D4 were then pumped in a vacuum line for 15, 60, 120, and 270 min, respectively. The final pressure was 0.06 torr in all cases. The data for day 15 are shown in Figure 11, and a more complete set has been included with the supporting information. The data show that excimer emission is strongest in the sample evacuated for only 15 min and weakest for the samples evacuated for 120 and 270 min. These results suggest that extended pumping increases the mobility of pyrene. As before, we believe that the effect is the result of the removal of residual hexane. We did not note any indication of pyrene loss in these experiments, although delayed luminescence studies (vide infra) may indicate minor loss of pyrene from the exterior surface. Clearly this is not enough to influence significantly the prompt luminescence.

Delayed Fluorescence. P-type delayed emission arises from triplet−triplet annihilation.[33−35] In the case of pyrene, this emission is frequently rich in the excimer component since the very nature of the process is such that it occurs only when two pyrene molecules come together.[28] To monitor delayed emission, we used a nanosecond laser pulse, which greatly facilitates instrumental timing sequences in the long time scales required for these studies. Further, we usually delayed the start time of the detection gate by either 0.5 or 1 μs since the prompt emission is otherwise so intense as to prevent the study of the weak delayed emission, which is always less than 0.1% of the intense early fluorescence. Due to instrumental limitations, it is impossible to fit both processes simultaneously within the dynamic range of the instrument with good signal-to-noise. Figure 12 shows the delayed fluorescence recorded from sample A1 on day 0. This emission decays with a lifetime of approximately 1 μs and is completely quenched by 1 atm of oxygen. The emission is present only under a very limited set of experimental conditions. Thus, it is essentially gone after 24 h and completely absent at later times. Further, pumping the sample under vacuum reduces and eventually eliminates this emission. While there may be some contribution from surface pyrene elimination, it is clear that other factors also contribute, since a similar effect is observed even when the sample is pumped at 77 K.

We believe (vide infra) that delayed emission is due to external surface pyrene molecules that are able to move far more

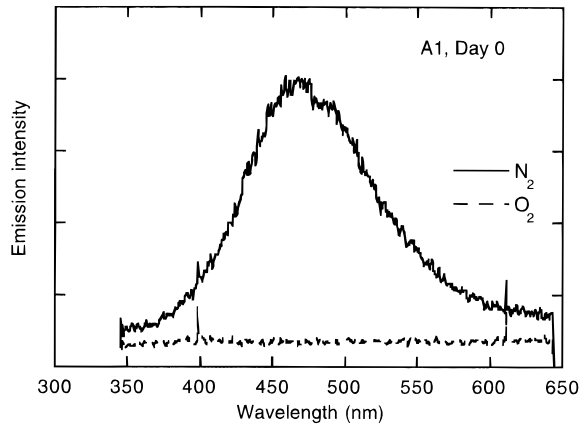


Figure 12. Delayed emission obtained upon 355 nm excitation of pyrene−NaY sample A1 (sealed with septum and purged with N_2 solid line) and O_2 (dashed line) prior to photolysis) day 0 after sample preparation using a 1 μs delay and a 1 μs gate.

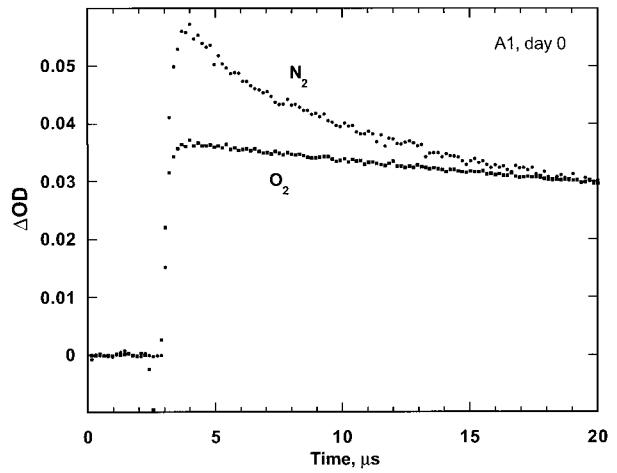


Figure 13. Time-resolved diffuse reflectance decay traces monitored at 440 nm obtained upon 355 nm excitation of pyrene−NaY sample A1 (sealed with septum and purged with N_2 (solid line) and O_2 (dashed line) prior to photolysis) day 0 after sample preparation.

rapidly than pyrene molecules within the interior lattice cages. We suggest that the disappearance of delayed emission after 24 h is due to the migration of molecules from the exterior surface into supercages. For reasons that remain unclear (perhaps hexane elimination from exterior cavities), the entry of pyrene appears to be facilitated under vacuum. Alternatively, one could attribute the delayed emission from surface sites some assistance by nitrogen, much in the way in which nitrogen appears to "lubricate" intercavity hopping. It appears unlikely that this effect would be as drastic as suggested by our observations.

Time-Resolved Diffuse Reflectance. These studies were performed using the same laser as in the previous section for 355 nm excitation. Pyrene triplets can be readily detected with laser flash photolysis technique by their characteristic absorption at around 440 nm.[36,37] In the case of opaque samples, such as zeolites, the technique of choice is time-resolved diffuse reflectance that does not require light to be transmitted through the sample.[22] Figure 13 shows decay traces monitored at 440 nm for sample A1 on day 0, under nitrogen and under oxygen. Clearly, there is a faster component, with a lifetime of ~0.8 μs that is completely eliminated by oxygen. In contrast, the main part of the decay remains essentially unaffected by oxygen and decays with a half-life of around 80 μs. This decay is not monoexponential, but its analysis was not pursued any further.

Interestingly, the fast oxygen-quenchable component decays with the same lifetime as the delayed emission discussed in the previous section; further, both are quenched by oxygen. Combined, these observations strongly suggest that delayed emission and fast triplet decay reflect the behavior of the same population of pyrene molecules. We propose that this population corresponds to a small fraction of the pyrene molecules present on the exterior surface of the zeolite crystals. We believe that this population eventually enters the interior of the zeolite lattice to occupy supercages. The fast component of the triplet decay was not observed on aged samples and was detected only on freshly prepared samples. The extent of the fast component corresponded to the amount of delayed emission observed in the emission experiments. The notion that these pyrenes originally reside on the surface is also consistent with the ready accessibility of these molecules to oxygen. These molecules are clearly more mobile than those that occupy the faujasite supercages.

Integrated View of the Behavior and Mobility of Pyrene in NaY. Global interpretation of the data presented in the preceding sections suggest that pyrene molecules incorporated on prebaked NaY at a 10% occupancy level have the following behavior.

(i) A few molecules remain on the exterior surface of the zeolite, despite repeated washing with clean hexane.

(ii) The molecules on this exterior surface are sufficiently mobile in the microsecond time scale to undergo triplet−triplet annihilation. The triplet lifetime for these molecules is significantly shorter than that for intracavity pyrene triplets. The same population responsible for delayed emission also accounts for the fast decay observed in diffuse reflectance studies.

(iii) The external molecules migrate toward the interior cavities during the first 24 h following inclusion. Most likely, the same diffusional processes that lead to delayed emission help those molecules locate accessible entries to the interior surface.

(iv) The majority of the pyrene molecules are located in the interior cavities after the few hours required for inclusion and sample preparation. However, their distribution is far from homogeneous, with double occupancy of the cavities greatly exceeding the statistical value. We believe that those cavities nearest the crystal surface are heavily populated, while those closer to the interior are largely vacant during the first few days following inclusion. This early distribution leads to dominant excimer emission in the case of fresh samples.

(v) No significant growth of excimer emission could be detected, other than a minor 20−25 ps delay. This implies that no intercavity migration takes place during our experiments, which is consistent with our observations that the complete aging of the sample requires almost 1 month. Since it is very unlikely that the ground-state pyrene molecules occupy the cavities in exactly the position required for excimer formation, we believe that intracavity motions, while perhaps minor, can occur in the picosecond time scale.

(vi) Intercavity migration of pyrene is a very slow process.[23] We systematically found that on day 15, the samples had not reached their final state. In fact, in many cases even after 1 month, the evolution may not have been complete. A very rough calculation based on particle size and a quadratic dependence between number of hops and distance traveled suggests that the "hopping time" for pyrene is in the 100 s time range.

(vii) Once the final statistical distribution has been achieved, the emission of the samples corresponds to essentially pure monomeric fluorescence.

TABLE 2: Sealing Procedure Employed for the Samples, All Sealed at 0.06 Torr

	vacuum desiccator treatment			
	15 min	1 h	2 h	4.5 h
room-temp vacuum quartz sealed	D1	D2	D3	D4

(viii) Poorly sealed (septum) nitrogen-saturated samples are virtually identical with those with other treatments (see Table 1) on day 0 but differ from sealed samples as aging progresses. We believe that these samples absorb ambient moisture and that eventually this water tends to limit intercavity pyrene migration.

(ix) In the case of sealed samples, we noted that pyrene is more mobile under nitrogen than under vacuum. This "lubricating" effect of nitrogen is tentatively assigned to site substitution allowing pyrene to migrate more easily. Clearly, this aspect deserves further examination with gases that absorb more or less readily than nitrogen.

(x) Residual hexane appears to have some mobility hindering effect, although not as pronounced as that of water. Residual hexane can be eliminated by prolonged vacuum pumping.

Conclusion

Our studies and the main points arising from it outlined above emphasize the importance of all aspects of the sample preparation protocol, including the dramatic effects of aging or the delay between sample preparation and analysis. It is clear that beyond a detailed description of the protocols used, authors in this field should establish whether samples have reached a stable situation in terms of probe distribution and spectroscopic properties, or whether such "aging" is still in progress. We note also that septum-sealed samples incorporate water if they are preserved for more than 1 day. Given that sealing by this method may not be reproducible and that ambient humidity changes from day-to-day and from site-to-site, only glass- or quartz-sealed samples may be durable enough in this respect. Pyrene, a spectroscopic probe that has been the frequent choice of researchers in organized systems, has proven quite useful in these systems. The properties measured in the case of triplet−triplet annihilation reflect real-time mobility, but all our other work simply uses pyrene as a probe to monitor mobility in very long time scales. Pyrene, having a short axis comparable to the window opening in faujasites, migrates very slowly among cavities, taking about 1 month to distribute randomly in a zeolite crystal of about 0.5 μm dimensions.

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Supporting Information Available: Extensive spectroscopic data and fluorescence lifetimes (20 pages). Ordering information is given on any masthead page.

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(20) The spectra of Figure 1 have been selected from among those presented in other figures. While introducing some duplication, this allows us to present early the main point of this article.
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