Photophysical Properties of Pyrene in Zeolites: A Direct Time-Resolved Diffuse Reflectance Study of Pyrene Anion Radicals in Zeolites X and Y

Xinsheng Liu, Kai-Kong Iu, and J. Kerry Thomas*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556 Received: February 23, 1994; In Final Form: May 11, 1994*

The formation of pyrene anion radicals (Py^{-}) in the supercage of different alkali-ion-exchanged zeolites X and Y was studied using direct time-resolved diffuse reflectance techniques. Many factors such as the Si/Al ratio, the nature of charge balancing cations, the preactivation temperature, the pyrene loading, the state of hydration, and the nature of the surfaces (external versus internal) were examined in order to understand the formation and stabilization of Py^{-} in these samples, and also the mechanism of the photoinduced electron transfer processes. The results show that photoinduced electron transfer does not occur from pyrene to pyrene in the zeolites but occurs between pyrene molecule and the acidic and basic sites of the zeolites. The basic sites of the zeolites, responsible for the formation of Py^{-} , are framework oxygen. Stabilization of Py^{-} requires the special environment of the zeolite supercage; it is noteworthy that Py^{-} cannot be formed on the external surface of a zeolite. The formation of Py^{+-} in the different alkali-ion-exchanged zeolites X and Y follows the order of basicity of these samples, which is calculated using the Sanderson electronegativity equalization principle. Preactivation of the samples at temperatures of 350, 550, and 750 °C does not affect the ratio of the anion to cation, Py^{+-}/Py^{++} , yields. Posthydration of the samples alters the photophysical processes in the zeolites and gives rise to an increase in the yield of Py^{+-} . At low light intensities, the photoinduced electron transfer follows a single-photon mechanism.

Introduction

Zeolites are porous crystalline aluminosilicates with frameworks built of SiO₄ and AlO₄ tetrahedra through shared oxygen,¹ and like many other solids, zeolites contain both acidic and basic sites which are responsible for a variety of catalytic reactions.^{1–3} The acidic sites in zeolites, either Broensted or Lewis type, have been well documented.^{4–6} However, the basic sites, which are proposed to be of Lewis type and present in the form of framework oxygen, have not received much attention.^{7–10} The strength of the basic sites has been shown to be dependent on the Al content and the nature of the charge balancing cations.^{8,9}

The photophysical and photochemical processes of guest molecules in zeolites are markedly affected by the precise zeolitic structures, as the nature of the surface varies in each zeolite.11-17 Studies of the photophysical properties of pyrene in zeolites X and Y, monitored by fluorescence, excimer formation, and electron and energy transfer, demonstrate that pyrene molecules adsorbed in zeolite supercages experience a very polar environment. Photoexcitation of pyrene in zeolites to produce pyrene cation radicals occurs via one- and two-photon excitation.^{17c,e} The additional energy to allow one-photon ionization of the adsorbed pyrene molecules is provided by the zeolite environment, 17c,e where the electrons are trapped by clusters of Na⁺ cations and eventually exist in the form Na_4^{3+} . Recently, the presence of pyrene anion radicals was also found on excitation of zeolites containing pyrene.¹⁸ The formation of pyrene radical cations and anions in zeolites is due to the acidity and basicity of the zeolite. In this paper, a detailed study is presented on the formation and stabilization of pyrene anion radicals in different alkali-cationexchanged zeolites X and Y using time-resolved diffuse reflectance techniques. The electron transfer processes are also discussed.

Experimental Section

Zeolites. Na⁺ zeolites X and A were purchased from Aldrich with Si/Al ratios of 1.4 for zeolite X and 1.0 for zeolite A. Na⁺

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TABLE 1: Chemical Composition and Sanderson Electronegativity (S_z) of the Zeolites Used in This Study, together with the Partial Charge on the Framework Oxygen (δ_0)

sample	composition of unit cell	Sz	δο
zeolite X	Li46Na34Al80Si112O384	2.45	0.40
	K76Na4Al80Si112O384	2.36	-0.43
	Rb ₅₈ Na ₂₂ Al ₈₀ Si ₁₁₂ O ₃₈₄	2.30	-0.45
	Cs50Na30Al80Si112O384	2.25	-0.47
zeolite Y	Li27Na28Al55Si137O384	2.60	-0.35
	K50Na5Al55Si137O384	2.54	-0.37
	Rb37Na18Al55Si137O384	2.50	-0.39
	Cs32Na23Al55Si137O384	2.45	-0.40

zeolite Y was provided by UOP (Union Carbide and Limited) with a Si/Al ratio of 2.5. The 50–60% Li⁺, Rb⁺, and Cs⁺ and 90–95% K⁺ ion-exchanged zeolites X and Y were obtained through conventional ion exchange procedures of the corresponding Na⁺ forms. The alkali metal contents of the ion-exchanged zeolites were analyzed using atomic absorption spectroscopy and chemical analysis and are given in Table 1.

Chemicals. Pyrene (99%) from Aldrich was purified with a silica gel column, followed by recrystallization from *n*-pentane. *n*-Pentane (>99%, spectroscopic grade) was further dried with thermally activated molecular sieve 3A pellets. *N*,*N*-Dimethylaniline (99%) was also from Aldrich and used as received.

Sample Preparation. Pyrene was loaded into zeolites, which had been preactivated at 350-750 °C for 6 h, via adsorption from pyrene/*n*-pentane solutions. Typically, 0.5 g of the preactivated zeolite was added to 5 mL of *n*-pentane solvent in a vial, followed by the addition of 0.5 mL of 1.44×10^{-6} mol/mL pyrene in *n*-pentane. The suspension was shaken and then left in the dark overnight. The solid was separated from its supernatant by filtration, washed twice with 5 mL of *n*-pentane, and then transferred immediately to a cuvette. The sample was evacuated at 10^{-3} Torr for 5 h at room temperature before the measurements were performed. The pyrene concentration in the supernatant was analyzed using UV-vis spectrophotometry. The amount of pyrene adsorbed by the zeolite was calculated by subtraction of

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^{*} Author to whom correspondence should be addressed.

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Figure 1. Typical transient diffuse reflectance spectrum of a Py-K⁺ zeolite Y sample with a loading of 1×10^{-6} mol/g recorded 20 μ s after the laser pulse of wavelength of 337 nm. The zeolite was preactivated at 325 °C for 9 h.

the residual pyrene from the total original amount in the solution. For most sample, the pyrene added was completely adsorbed by the zeolite.

Instruments. Steady-state fluorescence spectra were recorded on a SLM SPE 500C fluorimeter with a 250 W xenon arc lamp. Steady-state diffuse reflectance UV-vis spectra were collected on a Varian Cary 3 UV-vis spectrophotometer. The detailed experimental arrangement for time-resolved diffuse reflectance measurements and light intensity measurements have been given elsewhere.^{17e} The time-resolved diffuse reflectance data were treated using the Kubelka-Munk equation and described by $1 - R_t$, where R_t is the ratio of reflectivity with and without laser excitation.

Measurements of Quantum Yields. The fluorescence quantum yields of ${}^{1}\text{Py}^{*}$ were measured by using a Cary 3 UV-vis spectrophotometer operating in the diffuse reflectance mode. The diffuse reflectance spectra of the samples were collected both under vacuum and under O₂ (the gas pressure of O₂ > 400 Torr), respectively. In vacuum the light measured by the PMT, I_{v} , corresponds to the fluorescence and to the light reflected. Under O₂ the fluorescence is quenched and the measured light, I_{a} , corresponds to that reflected by the sample. If the original light intensity is I_0 , the quantum yield, Φ_f , is given by

$$\Phi_{\rm f} = (I_{\rm v} - I_{\rm a})/(I_0 - I_{\rm a}) \tag{1}$$

A correction of 5% was applied for the different sensitivity of the phototube at the excitation wavelength of 328 nm compared to that of the emission wavelength region of 370–400 nm.¹⁹ The method was used for solutions of pyrene in cyclohexane where a $\Phi_{\rm f}$ of 0.65 ± 0.03 was measured, in excellent agreement with that in the literature,²⁰ where the value is 0.65.

Confidence in the method for measurement of the fluorescence quantum yield of solid samples is provided by the fact that the literature fluorescence yield of pyrene in cyclohexane is achieved. The method does not require separate measurements of the absorbed and emitted light by the sample and excludes the errors of such measurements.

Due to the difficulty of assessing precisely the light absorbed by solid samples under laser excitation, the quantum yields of other species, ³Py^{*}, Py^{*+}, and Py^{*-}, were measured using a comparison method which uses a Py/laponite (a synthetic clay) sample²¹ as a standard. The quantum yield of Py⁺⁺ in the standard sample, Py/laponite (in a 2 mm thick quartz cuvette), was measured under steady-state conditions using a UV-vis spectrophotometer for measurement of the yield of Py*+ and a SLM photofluorimeter for the monochromatic light source. The choice of Py/laponite sample as a standard was based on the fact that the photoproduced Py*+ can be stabilized by the surface of laponite for a long time (the half lifetime is about 75 h).²¹ The radiation light was 337 nm with a bandpass of 4 nm. The percentage of light absorbed by the Py/laponite sample was calculated from the difference of the light reflected/scattered by the samples with and without pyrene. For this measurement the sample surface was set to 45° to the incident light and to the SLM photodetector. The irradiation of the sample at 337 nm was performed with the sample surface perpendicular to the incident light, and the yield of Py*+ was measured using the UV-vis spectrophotometer, taking the sample without irradiation as the background. The bandpass of light of the UV-vis spectrophotometer was set to 1 nm to ensure the detection area to be within the area irradiated. A plot of the yield of Py*+ versus the irradiation time was then made, and the first linear part of the plot, which passes through zero concentration of Py⁺ at the time zero, was used to calculate the quantum yield. The total number of photons per unit time from the light source was measured using the ferrioxalate actinometer described in the literature.²² The quantum yield of Py*+ in Py/laponite obtained was 0.0085 \pm 0.0008 on the basis of the Py⁺⁺ solution extinction coefficient of $6.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.^{23b,24b} The Py/laponite sample was then taken as a standard for the laser photolysis, and the quantum yields of Py*+ in the Py/zeolite samples were obtained by comparison and, subsequently, the quantum yields of other species using the corresponding solution extinction coefficients of the species.

The quantum yield of pyrene triplet was examined separately using another method which uses xenon gas to enhance the intersystem crossing of ${}^{1}Py^{*}$ in the Li⁺ zeolite X, as done by Horrocks et al.²⁵ for the pyrene ethanol solution. Basically, the ratios of the optical densities $((OD)_{Xe}/(OD)_{v})$ of ${}^{3}Py^{*}$ and fluorescence intensities of ${}^{1}Py^{*}$ (F_{0}/F) in the Py-Li⁺ zeolite X sample were measured under vacuum and under different pressures of Xe gas. The quantum yield of ${}^{3}Py^{*}$ under vacuum, Φ_{T} , can be calculated using the equation below by plotting F_{0}/F



Figure 2. Transient diffuse reflectance spectra of Py-K⁺ zeolite X (pyrene loading is 1.5×10^{-6} mol/g) with different amounts of DMA (+5 × 10⁻⁵ mol/g, 2 × 10⁻⁴ mol/g) recorded 20 µs after the laser pulse. The zeolite was preactivated at 325 °C for 9 h. Insert: Time-resolved diffuse reflectance signals of Py-DMA-K⁺ zeolites Y monitored at 470 nm (up line) and 490 nm (down line), respectively.

versus
$$[(OD)_{Xe}F_0/(OD)_v F - 1]$$

$$F_0/F = [(OD)_{Xe}F_0/(OD)_{V}F - 1]\Phi_T + 1$$
 (2)

The overlapping of spectra was corrected by admitting a low pressure of O_2 (~ 60 Torr) which reacts efficiently to remove ³Py* and Py^{•-} and leaves Py^{•+} unchanged. The quantum yield of ³Py* obtained from this method was 0.031, which is reasonably in agreement with the value obtained for this sample, ~0.01, using the comparison method (see Table 5).

The biggest criticism of this method of measuring the quantum yields of ³Py*, Py*+, and Py*- is the use of the solution extinction coefficients of these species.

Results and Discussion

Stabilization of Py-. Figure 1 shows a typical diffuse reflectance spectrum of a Py zeolite sample (Py-K-Y) with $1 \times$ 10⁻⁶ mol/g pyrene loading, excited with laser pulses of wavelength 337 nm; the spectrum was recorded 20 μ s after the laser pulse. Four bands at 410, 450, 490, and 520 nm are observed in the spectrum; the bands at 410 and 520 nm are assigned to the pyrene triplet (³Py^{*}), the band at 450 nm to the pyrene cation radical (Py^{+}) ,^{23,24} and the band at 490 nm to the pyrene anion radical (Py*-).^{18,25,26} The presence of Py*- in zeolites has been identified by a series of experiments, such as its removal by O_2 and its insensitivity to ammonia and N,N-dimethylaniline (DMA).¹⁸ The basic sites in the zeolite cavities provide suitable conditions and environments for the formation and stabilization of Py-. The e- transfer from the basic sites of zeolites to excited pyrene is akin to simpler systems such as the e- transfer from DMA to excited pyrene.

The pyrene anion radicals in zeolites may be identified by its direct production via an electron donor such as DMA. Figure 2 gives laser-excited transient diffuse reflectance spectra of Py zeolite KX samples with different amounts of co-adsorbed DMA on laser excitation. With high concentrations of DMA (2×10^{-4}

mol/g), four bands are observed in the spectrum at 390, 420, 470, and 490 nm. The band at 390 nm is due to ³DMA^{*},²⁸ while the bands at 420, 470, and 490 nm are attributed to ³Py*, DMA*+, and Py^{-.26,27} For samples with low DMA content (5 \times 10⁻⁵ mol/g), the 390 nm band is weak. It is seen from Figure 2 that increasing the concentration of DMA in the zeolite increases the intensities of the DMA⁺⁺ and Py⁺⁻ adsorptions. Steady-state fluorescence studies reveal that there are three different species in the Py-DMA zeolite KX sample: excited monomer pyrene, excited DMA, and the pyrene-DMA exciplex (emission spectrum not shown). The presence of the exciplex suggests that some pyrene and DMA molecules are located in close proximity. Excitation at 337 nm promotes electron transfer from DMA to pyrene and leads to formation of DMA*+ and Py*-. A direct back-electron transfer from Py- to DMA++ is seen in the insert of Figure 2, where identical decay rates for both species are observed. The surface of the zeolite provides an environment which stabilizes the charged species formed, a fact which has also been observed for other ion pairs, as demonstrated by the studies of Kochi et al.15

With zeolite systems which do not contain electron donors such as DMA, the observed electron transfer processes are controlled by the acidic and basic sites of the zeolites. A good example is the photoionization of pyrene in zeolites, forming pyrene cation radicals and electrons trapped by clusters of Na⁺ cations.^{17e} The present studies illustrate the dual role played by excited pyrene molecules in zeolite supercages. On excitation, pyrene molecules present in the supercages act as electron donors and as electron acceptors. Direct electron transfer from excited pyrene to another pyrene does not occur, but e⁻ transfer from the pyrene to acidic sites giving the cation radical and e- transfer from basic sites to pyrene giving the anion radical occur.¹⁸ No pyrene excimer is observed in steady-state fluorescence studies, which suggests that the acidic and basic sites probed by the pyrene molecules are unlikely to be located in the same supercage. We therefore conclude that two kinds of supercages are present in the zeolites: acidic supercages where excited pyrene forms cation



Figure 3. Time-resolved emission decay of pyrene in Li⁺, K⁺, Rb⁺, and Cs⁺ zeolites X (from slow decay to fast decay) monitored at 400 nm. The smooth lines are curve-fitted lines using the Gaussian distribution model.³⁰ The zeolites were preactivated at 550 °C for 8 h. The pyrene loading was $2.8 \times 10^{-6} \text{ mol/g}$.

TABLE 2: Apparent Yields of ${}^{3}Py^{*}$ (410 nm), Py⁺⁺ (450 nm), and Py⁺⁻ (490 nm) in Li⁺, K⁺, Rb⁺, and Cs⁺ Ion-Exchanged Zeolites X and Y^{*}

sample	³Py*	Py*+	Py•−	Py*-/Py*+
LiX	0.082	0.150	0.085	0.57
KХ	0.072	0.137	0.127	0.93
RbX	0.082	0.137	0.140	1.02
CsX	0.147	0.147	0.163	1.11
LiY	0.033	0.074	0.044	0.59
KY	0.030	0.075	0.077	1.03
RbY	0.040	0.076	0.088	1.16
CsY	0.111	0.086	0.101	1.17

^a The yields are obtained using the Kubelka–Munk equation and described by $1 - R_t$, where R_t is the ratio of reflectivity with and without laser excitation. Pyrene loading is 2.8×10^{-6} mol/g.

radicals (acidic environment) and basic supercages where excited pyrene forms anion radicals (basic environment).

Factors Affecting Formation of Py^{-} . Several factors such as the Si/Al ratio, the nature of cations, the preactivation temperature, the pyrene loading, the state of hydration, and the nature of the surfaces (external versus internal) were examined to fully understand the formation of Py^{-} in zeolites. The results are given below.

a. Si/Al Ratio. The effect of the Si/Al ratio on the formation of Py^{•-} can be seen by a comparison of zeolites X and Y which have identical framework topology. Table 2 shows the transient diffuse reflectance intensities of ${}^{3}Py^{*}$, Py^{•+}, and Py^{•-}, recorded 20 μ s after laser pulse, for both Py-M⁺ zeolites X and Y (M⁺ = alkali cations) with the same pyrene loading. The data clearly show that a high yield of Py⁺⁻ is formed on zeolite X compared to zeolite Y, which is consistent with the difference in basicity of the two zeolites (zeolite X > zeolite Y).⁹

b. Nature of Charge-Balancing Cations. The effect of cations on the yields of pyrene products was examined for various zeolites with different alkali cations such as Li^+ , K^+ , Rb^+ , and Cs^+ . The

Na⁺-form zeolite samples were excluded because of overlapping of the Py^{*-} band with that of Na₄³⁺ clusters formed in the Py-Na⁺ zeolites X and Y.^{17e} Time-resolved fluorescence studies of Py zeolite X samples (see Figure 3) show that the half-life of ¹Py*, measured via its fluorescence, decreases in the order of Li+ $(86 \text{ ns}) > \text{K}^+ (44 \text{ ns}) > \text{Rb}^+ (9.4 \text{ ns}) > \text{Cs}^+ (2.5 \text{ ns})$; the zeolite Y samples follow exactly the same order as zeolite X. The shortening of the fluorescence lifetime can be understood on the basis of the heavy atom effect theory, as demonstrated by Ramamurthy et al.¹³ Table 2 shows the intensities (or product yields) of time-resolved diffuse reflectance signals of Li⁺, K⁺, Rb⁺, and Cs⁺ zeolites X and Y monitored at 410 nm for ³Py⁺, 450 nm for Py⁺⁺, and 490 nm for Py⁺⁻. An increase in the yield of ³Py^{*} for samples with heavy atoms is clearly seen and is due to the heavy atom effect. The yield of ³Py* increases from K* to Cs⁺, and the highest intensity is seen for the Cs⁺ zeolites. The yields of Py⁺⁺ in Li⁺, K⁺, Rb⁺, and Cs⁺ zeolites are similar, but those of zeolites X are larger than those of zeolites Y. However, the yields of Py⁻ in both zeolites follow the same sequence of Cs⁺ $> Rb^+ > K^+ > Li^+$, the Py- yields of zeolite X being larger than those of zeolite Y.

An understanding of the experimentally observed trends requires a knowledge of the nature of the sites which accept and donate electrons. From the literature, ⁷⁻¹¹ it is expected that the electron-donating sites, which are responsible for Py[•], should be the basic sites present in the form of framework oxygen. There may be several electron-accepting sites, but only that of Na₄⁴⁺, i.e., clusters of charge-balancing cations, is directly observed.^{17e} If these sites are indeed responsible for the observed pyrene anions and cations, then the observed trends should follow the basicity and acidity of the zeolites. For the basicity of the zeolites, the charges on the framework oxygens were calculated using the Sanderson electronegativity equalization principle,²⁹ which has been successfully used to describe acidities and basicities of zeolites.^{9,30,31} According to Sanderson,²⁹ the intermediate electronegativity of zeolites (S_z) with a composition of



Partial Charge on Framework Oxygen

Figure 4. Plots of the yields of Py^{-} and Py^{+} against the partial charge on framework oxygen of Li⁺, K⁺, Rb⁺, and Cs⁺ zeolites X and Y.

 $M_y Na_{x-y} Al_x Si_{192-x} O_{384} \ (x \ge y)$ is

$$S_{z} = (S_{Si}^{192-x} S_{Al}^{x} S_{O}^{384} S_{Na}^{x-y} S_{M}^{y})^{1/(192+384+x)}$$
(3)

Here, M = Li, K, Rb, and Cs, and z = zeolite. From the intermediate electronegativity of zeolites together with the Sanderson electronegativity of the elements, the partial charge (δ_0) on the framework oxygen (measure of the basicity) of the zeolites can be calculated as

$$\delta_{\rm O} = (S_{\rm z} - S_{\rm O}) / 1.57 S_{\rm O}^{-1/2} \tag{4}$$

The results are given in Table 1. The plots of the yields of Py^{-} against the partial charge of the framework oxygen are shown in Figure 4. The linear relationship between the yield of Py^{-} and the charge of the framework oxygen for both zeolites X and Y strongly indicates that formation of Py^{-} in the zeolites is directly related to the basicity of the zeolites.

The decays of the time-resolved diffuse reflectance signals of Py^{-} and Py^{+} in a series of zeolite X samples are examined in the 10 ms region, and the results show that the decay of Py^{+} is slow for Li⁺ zeolites and increases in the order of Li⁺ < K⁺ < Cs⁺ < Rb⁺, while for Py^{-} the slowest decay is observed for the Cs⁺ zeolites and increases as Cs⁺ < K⁺ ~ Rb⁺ < Li⁺. The Py-M⁺ zeolites Y exhibit similar trends. These trends are consistent with the acidities and basicities of the zeolites,^{8,9} and with their acid-base catalytic properties as illustrated by reactions such as

toluene +
$$CH_3OH \rightarrow xy$$
lene (on acidic zeolites Li^+ -
X and Li^+ -Y)

 \rightarrow styrene + ethylbenzene

(on basic K^+ , Rb^+ , and Cs^+ zeolites X and Y)^{32,33}

The decays of Py^{*+} and Py^{*-} do not follow the sequence K^+ , Rb^+ , and Cs^+ and may be due to the degree of ion exchange of the samples (see Table 1). The decay rates for the Py^{*-} and Py^{*+} in the same zeolite are quite different, indicating that direct backelectron transfer from Py^{*-} to Py^{*+} does not occur, and that Py^{*-} and Py^{*+} behave independently in these systems.

The ratio Py^{-}/Py^{+} also gives the same trends, which follows the basicity of the zeolites (Table 2).

c. Preactivation Temperature. Three temperatures, 350, 550, and 750 °C, were employed for activation of the Cs⁺ zeolite Y samples, and the ratio of Py^{-}/Py^{+} was measured (see Table 3). The data in Table 3 show that, within experimental error, the ratios of Py^{-}/Py^{++} for these samples, preactivated at different

 TABLE 3:
 Effects of Preactivation Temperature of the Zeolites on the Ratio Py*-/Py*+

sample	preactivation temp (°C)	lifetime of ¹ Py* (ns)	Py•-/Py•+
Py-Cs ⁺ -Y	350	2.2	1.29
•	550	2.4	1.33
	750	2.4	1.17

^a Pyrene loading is $1.4 \times 10^{-6} \text{ mol/g}$.

 TABLE 4:
 Effects of Hydration on Yields of the Species in Zeolites Y

	yield ratios	of hydrated to vacu	um samples
sample	³ Py*	Py*+	Py*-
LiY	2.85	1.22	0.84
KY	0.72	1.09	1.13
RbY	0.92	1.04	1.09
CsY	1.22	1.32	1.30

temperatures, are nearly identical. This indicates that, over this temperature rangee, the acidities and basicities of the zeolites are not significantly changed.

d. Pyrene Loading. Different pyrene loadings were employed for both zeolites Cs⁺-X and -Y in the range from 1×10^{-6} to 7×10^{-6} mol/g. Figure 5a,b gives plots of the yields of Py⁻⁻ and Py^{*+} as a function of pyrene loading in zeolites X and Y. Both Py*- and Py*+ increase on increasing the pyrene loading, and the decay of these species also changes with pyrene loading. Figure 5c,d shows the plots of the decay rates (obtained by curve fitting as in Figure 3 using the Gaussian model³⁴) against pyrene loading. The general trend observed is that the decay rates increase as the pyrene loading increases for both Py*+ and Py*-. This general trend probably reflects changes of the acid and base strength of the sites experienced by pyrene molecules as the pyrene concentration increases in the zeolites. The stronger acidic and basic sites lead to more stable Py⁺⁺ and Py⁻⁻ species in the zeolites, while the weaker acidic and basic sites lead to less stable Py⁺⁺ and Py*-. An additional cause which leads to the increased decay may result from the direct back-electron transfer between the Py^{*+} and Py^{*-} species when the pyrene concentration is high.

e. Posthydration of Zeolites. The effect of hydration of the samples on the formation of Py-- and Py++ was examined for zeolites Y with different cations under conditions where water vapor (6 Torr) was introduced into the Py-M zeolites ($M = Li^+$, K⁺, Rb⁺, Cs⁺). The intensity ratios of time-resolved diffuse reflectance before and after adsorption of water are shown in Table 4. It is clearly seen, from Table 4, that the posthydration of the Py-M zeolites changes the yields of ³Py*, Py*+, and Py*-. This indicates that the posthydration of these samples modifies the environments experienced by the pyrene molecules and also alters the photophysical and photochemical processes.^{17b,c,e} The changes depend on the nature of the charge-balancing cations. For Py-Li⁺-Y, posthydration increases the yields of ³Py^{*} and Py^{+} but decreases that of Py^{-} (see Table 4), while for $Py-K^{+}$ -, and Rb+-Y, posthydration decreases the yield of 3Py* but increases those of Py++ and Py--. However, for Py-Cs+-Y, the posthydration increases the yields of all three species. The changes occurring in the posthydration are complex and involve many processes such as solvation of the charge-balancing cations, weakening of the interactions between the charge-balancing cations and the framework oxygens, and modification of the acidity and basicity of zeolites. These processes not only change the photophysical processes as observed from the above yield change, but also change the electron-trapping sites. For the posthydrated samples, the electrons are trapped by the adsorbed water molecules, rather than by the clusters of the charge-balancing cations.^{17c,e}

f. Nature of the Surfaces. It is well established that adsorbed molecules such as pyrene are located inside the supercages¹⁷ and interact with the surface of the supercage. To understand whether this particular environment is critical for the formation of Py^{-} , photoexcitation of pyrene on the external surface of zeolites was



Figure 5. Plot of yield (a, top left; b, top right) and decay rate (c, bottom left; d, bottom right) of Py^{-} and Py^{+} in $Py-Cs^{+}$ zeolite X and Y as a function of pyrene loading. The zeolite was preactivated at 550 °C for 6 h.



Figure 6. Transient diffuse reflectance spectrum of the Py-NaA sample. The spectrum was taken 10 μ s after the laser pulse of wavelength of 337 nm. Pyrene loading is $7.4 \times 10^{-7} \text{ mol/g}$. Pyrene emission studies show that no pyrene excimers are present on the external surface of the zeolites. The zeolite NaA was preactivated at 550 °C for 6 h.

examined. Due to the large entry aperture of the zeolites X and Y, zeolite NaA was chosen for this purpose as pyrene is solely located on the external surface of this zeolite. The reasons for choosing zeolite A are the following: (1) structurally, it is related to zeolites X and Y (all have sodalite cages as building units), and the α cage in zeolite A is only slightly smaller than the supercage in zeolites X and Y (11 versus 13 Å in diameter);¹ (2) the small entry aperture (4 Å) does not allow pyrene to enter the α cage, and the pyrene molecules are located only on the external surface of zeolite A; (3) the framework Si/Al ratio is similar to

that for zeolite X (1.0 versus 1.4); (4) chemically, the lower Si/ Al ratio of zeolite A should favor the formation of Py^{-} , provided that the formation of Py^{-} does not require a special environment. Figure 6 shows a transient diffuse reflectance spectrum of the $Py-Na^+$ -A sample. Three bands at 410, 450, and 550 nm are seen in the spectrum and correspond to ³Py^{*}, Py⁺⁺, and trapped electrons, respectively.^{17e,23,24} The characteristic absorption of Py^{-} at 490 nm is not seen. The absence of the 490 nm band in the spectrum clearly demonstrates that no pyrene anion radicals are formed on the external surface of the zeolite. We conclude



Figure 7. Changes of the yield of Py⁻ as a function of excitation light intensity for Py-K⁺ (a, top) and Py-Cs⁺ (b, bottom) zeolites X and Y. The zeolites were preactivated at 500 °C for 6 h. Pyrene loading is 5.8 $\times 10^{-6}$ mol/g.

TABLE 5: Quantum Yields of the Observed Species⁴

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sample	¹ Py*	³ Py*	Py*+	Py⊷
Li-X	0.61	0.0093	0.0096	0.0035
K-X	0.41	0.0082	0.0088	0.0053
Rb-X	0.11	0.0093	0.0088	0.0058
Cs-X	Ь	0.0147	0.0094	0.0068
Li-Y	0.40	0.0038	0.0048	0.0018
K-Y	0.11	0.0034	0.0048	0.0032
Rb-Y	0.07	0.0046	0.0049	0.0037
Cs-Y		0.0126	0.0055	0.0042

^a The errors of the data given in the table are within 10%. ^b The data cannot be obtained by the method mentioned in the experimental section.

that the formation and stabilization of Py^{-} requires a selective environment, that exists only in the supercage.

In contrast to Py^{-} , Py^{+} is readily formed in the zeolite A system and exhibits the strongest absorption signal in the spectrum. Unlike Py^{-} , Py^{++} can be formed in a variety of different environments due to one- and two-photon excitation. O₂ reduces the Py^{+} yield, indicating a multiphoton mechanism; this is in contrast to the single-photon mechanism observed for pyrene encased inside zeolites X and Y (see below and ref 17e).

The presence of the 550 nm band in the spectrum indicates that electrons are trapped by clusters of Na⁺ cations in the sodalite cage, the electron penetrating through the surface into cages where it is trapped. The low intensity of the signal of the trapped electrons compared to that of Py^{*+} implies the presence of other electron-trapping sites on the external surface, which are not seen in the spectral region studied. A detailed discussion is given elsewhere.³⁵

Photoinduced Electron Transfer Mechanism. Previous studies^{17e} have shown the presence of a single-photon ionization process for electron transfer from excited pyrene to clusters of Na⁺ cations, forming Py⁺⁺ and Na₄³⁺. The mechanism of the photoinduced

electron transfer from basic sites of the zeolite to excited pyrene to form Py^{-} was examined by varying the light intensity. Figure 7 shows the changes in the yield of Py^{-} as a function of intensity of excitation light for the $Py-K^+$ and Cs^+ zeolites X and Y. For $Py-K^+$ zeolites X and Y (Figure 7a), the Py^{-} yields are linear with light intensity, while for $Py-Cs^+$ zeolites X and Y (Figure 7b), the Py^{-} yields tend to reach a plateau at light intensities greater than 4 mJ/cm². The linear relationships observed in Figure 7 suggest that formation of Py^{-} in the supercage follows a single-photon excitation.

The processes occurring on excitation of Py zeolite systems can be pictured as follows:



Py: Pyrene; A: Acidic sites; B: Basic sites; N: Neutral sites Active channels without gas molecules; Active channels when NH₃ is present; Possible active channels when NH₃ is present.

On excitation, three reaction channels are present which produce the observed species. The pyrene molecules adsorbed on the neutral sites of the zeolite (Py/N) form $^{1}Py^{*}$ via absorption of one photon and Py*+ via absorption of two photons. The 'Py* then forms ³Py* through intersystem crossing. The pyrene molecules adsorbed on the acidic sites of the zeolite (Py/A) form Py⁺⁺ via absorption of one photon, while those adsorbed on the basic sites of the zeolite (Py/B) form Py- also via absorption of one photon. The reaction channels perform independently in the system but are controlled by the nature of the surface, the hydration state of the zeolite, and the nature of the chargebalancing cations. Introducing quencher molecules such as O₂ and NH₃ blocks certain reaction channels. For example, in the presence of O_2 , only the reaction channels of $Py/A \rightarrow Py^{+}$ (onephoton process) and $Py/N \rightarrow {}^{1}Py^{*}$ are active. 17e However, in the presence of NH₃, the reaction channel of $Py/A \rightarrow Py^{+}$ is not present, but the reaction channels $Py/B \rightarrow Py^{-}$ and $Py/N \rightarrow$ $^{1}Py^{*} \rightarrow ^{3}Py^{*}$ are still operational (see the picture above). Monitoring changes of the yields in Py-Cs⁺ zeolite Y in the presence of NH₃, by using steady-state and time-resolved fluorescence and time-resolved diffuse reflectance spectroscopy, shows that yields of ³Py* and ¹Py* are both increased, but to different extents (1.54-fold increase for ³Py* versus 1.27-fold increase for ¹Py*), while the yield of Py*- is unaffected by NH₃. These data show that NH₃ alters the acidic site but has little effect on the other sites. The increased yields of ³Py* and ¹Py* are indicative of a change in population of Py/N and a destabilization of the ions at the active sites; in other words, neutralization of Py*+ by the negative species (e-) leads to 'Py* and ³Py*. Ideally, the latter process should lead to ³Py* and ¹Py* in a ratio of 3:1, compared to a ratio of 2:1 found experimentally, and therefore it is suggested that both reaction channels are operational. The quantum yields of these species were measured and are summarized in Table 5. It is pertinent to note that NH_3 gas has no effect on the lifetime of $^1Py^*$.

In comparison with the quantum yields of pyrene in solution,²⁰ it is seen from Table 5 that the quantum yields of ${}^{3}Py^{*}$ in the zeolites are very low. This low quantum yield of ${}^{3}Py^{*}$ suggests

that the intersystem crossing of ¹Py* to ³Py* is somehow prohibited. This is verified by the temperature effect studies on the intersystem crossing where no significant lifetime change of ¹Py* is observed for the Py-Na⁺ zeolite samples at room temperature and 77 K, which is different from what was seen for the pyrene solution.36

In summary, zeolites provide a variety of "active" sites which influence photophysical and photochemical reactions. The Lewis acid sites such as the ionic clusters Na_4^{4+} act as electron acceptors, and the basic sites such as framework oxygen act as electron donors. The unique environment provided by the zeolite supercage is essential for the observed photophysical and photochemical events, particularly the electron-donating properties of the zeolites and stabilization of the negatively charged species such as Py*-. The photoevents may also be used to comment on various active sites which are not accessible by other techniques.

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