

## FLUORESCENCE STUDIES OF PYRENEALDEHYDE ADSORBED WITHIN ZEOLITE SUPERCAGES

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### Summary

The absorption and fluorescence of pyrenealdehyde have been utilized to probe the nature of sites in solid zeolites that adsorb aromatic molecules. In addition to substantial spectral shifts, excimer formation is found for pyrenealdehyde adsorbed on type Na<sup>+</sup>-Y zeolites. A similar enhancement of excimer formation is noted for  $\gamma$ -cyclodextrins in aqueous solutions of pyrenealdehyde.

### 1. Introduction

Zeolites are ordered three-dimensional aluminosilicates composed of pores whose molecular dimensions control the structures of species that may enter and exit the zeolite, the aggregation properties of species adsorbed by the zeolite and the dynamics of species adsorbed by the zeolite [1]. Although the importance of zeolites as industrial catalysts for organic reactions is broadly appreciated and interest in photochemistry of substrates on solid surfaces has expanded considerably [2 - 5], the photochemistry and photophysics of organic molecules adsorbed on zeolites are sparse [6].

Our interest in exploring photoprocesses on zeolite surfaces stems from a comparison of the inner cavity supercages [7] for type A and type Y zeolites with those of cyclodextrin cavities [8]. We describe below our results concerning excitation of pyrenealdehyde (a fluorescent probe known to be sensitive to environmental parameters [9 - 11]) adsorbed to type Y zeolites.

### 2. Experimental results and discussion

Pyrenealdehyde adsorbed by the three type Y zeolites utilized in this study (Na<sup>+</sup>-Y, NH<sub>4</sub><sup>+</sup>-Y and H<sup>+</sup>-Y) showed bathochromic spectral shifts

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when compared with the absorption spectra obtained in homogeneous solutions<sup>†</sup>. (The zeolites Na<sup>+</sup>-Y, NH<sub>4</sub><sup>+</sup>-Y and H<sup>+</sup>-Y were purchased from Alfa Ventron, Beverly, MA, and supplied as LZ-Y52, LZ-Y62 and LZ-Y72 respectively. The surface areas supplied by the manufacturer are 900 m<sup>2</sup> g<sup>-1</sup>, 948 m<sup>2</sup> g<sup>-1</sup> and 730 m<sup>2</sup> g<sup>-1</sup> respectively.) The lowest energy absorption maxima are about 400 nm on type Na<sup>+</sup>-Y and NH<sub>4</sub><sup>+</sup>-Y zeolites compared with 391 nm and 394 nm for pyrenealdehyde dissolved in pentane and methanol respectively. The bathochromic shifts are typical of carbonyl chromophores adsorbed to polar surfaces [12] and are a manifestation of the forces responsible for adsorption [13].

The absorption spectrum for pyrenealdehyde adsorbed to type H<sup>+</sup>-Y zeolite is considerably bathochromic ( $\lambda_{\max} \approx 420$  nm) compared with adsorption to other surfaces. Bathochromic spectral shifts are also observed with the addition of tin(IV) chloride (10<sup>-2</sup> M) to pyrenealdehyde (3 × 10<sup>-5</sup> M) dissolved in methylene chloride ( $\lambda_{\max} \approx 420$  nm).

The front-face emission<sup>†</sup> of pyrenealdehyde, adsorbed to the type Na<sup>+</sup>-Y (NH<sub>4</sub><sup>+</sup>-Y) zeolite, was observed to have a fluorescence maximum at 460 nm (465 nm) with the lowest energy excitation maximum at 400 nm (400 nm). In addition, the emission maxima were 468 nm, 470 nm and 470 nm for pyrenealdehyde adsorbed to alumina (neutral), florisil and freeze-dried silica (mean pore diameter, less than 20 Å; surface area, 951 m<sup>2</sup> g<sup>-1</sup>) [14] respectively. The monomer excited state lifetime was typically  $(4 \pm 1) \times 10^{-9}$  s for all the systems studied [9].

Pyrenealdehyde adsorbed to type Na<sup>+</sup>-Y zeolite also revealed a fluorescence band with a maximum at 560 nm (Fig. 1). The contribution of this bathochromic band to the total emission increased with increasing surface coverage (the area of a molecule of pyrenealdehyde was assumed to be 100 Å<sup>2</sup>) (Fig. 1). A similar emission (Fig. 2) with a fluorescence maximum at 580 nm was observed with addition of  $\gamma$ -cyclodextrin to aqueous pyrenealdehyde solution (10<sup>-6</sup> M). The emission at 560 and 580 nm for pyrenealdehyde adsorbed to type Na<sup>+</sup>-Y zeolite and included within  $\gamma$ -cyclodextrin was assigned to pyrenealdehyde excimer fluorescence [11]. No excimer emission was observed with adsorption (with surface coverage up to 20%) of pyrenealdehyde by freeze-dried silica [14], chromatographic silica and florisil. The ratio  $I_E/I_M$  of excimer to monomer emission for pyrenealdehyde ( $1 \times 10^{-9}$  moles per milligram of support) adsorbed to type Na<sup>+</sup>-Y (about

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<sup>†</sup>All the supports used in these studies were used without prior treatments. Samples were impregnated by suspending the support (about 500 mg) in 2 ml of probe dissolved in pentane (about 10<sup>-4</sup> - 10<sup>-5</sup> M). The samples were allowed to sit for at least 1/2 h, the solvent was removed under a vacuum nitrogen stream and the samples were pumped dry by overnight evacuation. The absorption spectra were obtained on a Perkin-Elmer 559A UV-VIS spectrophotometer using an internal integrating sphere. The front-face fluorescence was monitored using a Spex Fluorolog spectrophotometer. For pyrenealdehyde, all excitations were performed at 380 nm. The fluorescence lifetimes were obtained by single-photon counting (Photochemical Research Associates Inc., West London, Ontario) using a pulse lamp (halfwidth,  $2 \times 10^{-9}$  s).

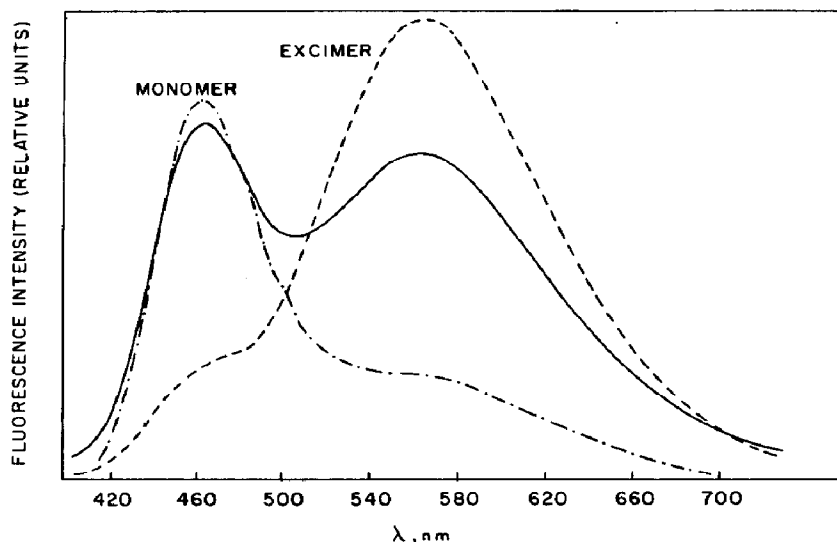


Fig. 1. Fluorescence emission of pyrenealdehyde adsorbed to type  $\text{Na}^+$ -Y zeolite at various surface coverages: ---, 0.07%; —, 0.22%; - · - ·, 0.36%.

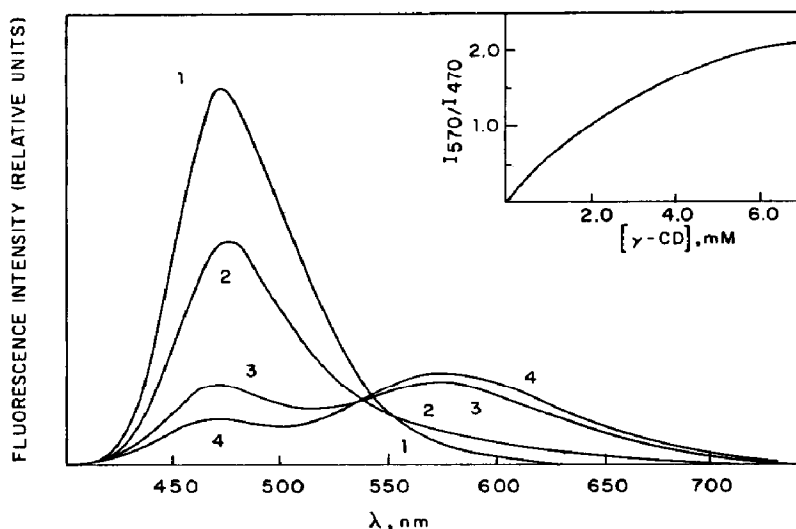


Fig. 2. Fluorescence emission of pyrenealdehyde in water and with the addition of various concentrations of  $\gamma$ -cyclodextrin: curve 1, 0.0 mM; curve 2, 0.2 mM; curve 3, 1.9 mM; curve 4, 6.9 mM.

0.1% surface coverage),  $\text{NH}_4^+$ -Y zeolite (about 0.1% surface coverage) and alumina (about 1% surface coverage) was 0.41, 0.29 and 0.14 respectively. In all cases, the excitation spectra for the monomer and excimer emission were similar except for a 5 - 10 nm bathochromic shift when the excimer emission was monitored. The excimer emission lifetime was  $14 \times 10^{-9}$  s for pyrenealdehyde adsorbed to type  $\text{Na}^+$ -Y zeolite and  $19 \times 10^{-9}$  s for the pyrenealdehyde- $\gamma$ -cyclodextrin inclusion complex.

The front-face emission obtained with excitation of pyrenealdehyde adsorbed to type H<sup>+</sup>-Y zeolite resulted in an emission with a maximum at 513 nm, with an excitation maximum at 450 nm. The emission lifetime was less than  $2 \times 10^{-9}$  s<sup>†</sup>. When the type H<sup>+</sup>-Y zeolite was impregnated with pyrenealdehyde (surface coverage, about 0.25%) in the presence of pyridine or atmospheric moisture, only the pyrenealdehyde monomer emission was observed. The 513 nm emission is assigned to the radical cation of pyrenealdehyde that forms with adsorption by the type H<sup>+</sup>-Y zeolite. An identical emission was obtained with excitation of pyrenealdehyde dissolved in methylene chloride ( $3 \times 10^{-5}$  M) in the presence of tin(IV) chloride ( $10^{-2}$  M).

The monomer fluorescence maxima for pyrenealdehyde adsorbed to the three type Y zeolites all indicate, as expected, exposure of the fluorophore to a polar environment [9, 10]. The pyrenealdehyde excimer-type fluorescence also appears to be sensitive to solvent polarity [11]. For example, the excimer emission maxima are 530 nm, 550 nm, 560 nm, 565 nm and 580 nm for pyrenealdehyde in or on heptane [11], acetonitrile [11], type Na<sup>+</sup>-Y zeolite, ethanol [11] and  $\gamma$ -cyclodextrin solution respectively. The excimer emission maximum for pyrenealdehyde adsorbed to Na<sup>+</sup>-Y zeolite is hypsochromic, as is its monomer emission maxima, compared with that obtained with  $\gamma$ -cyclodextrin solutions. These comparisons reveal a non-hydrophilic nature to the binding within the zeolite supercage.

The type Na<sup>+</sup>-Y zeolite is a very effective surface for enhancing pyrenealdehyde excimer fluorescence especially when our inability to obtain it on silica (even at increased surface coverages) is considered. We believe that within the zeolite (and cyclodextrin) cavities, the population of monomer pyrenealdehyde units oriented in the excimer geometry is increased. We have similarly observed an enhancement in the intramolecular excimer emission accompanying adsorption of 1,3-bis( $\beta$ -naphthyl)propane to Na<sup>+</sup>-Y zeolite (compared with freeze-dried silica adsorption) [15].

The type H<sup>+</sup>-Y zeolite was the only adsorbent for pyrenealdehyde in which an emission assigned to a ground state radical cation was observed. The involvement of ground state oxidation is supported by the absorption, excitation and emission spectral shifts obtained with pyrenealdehyde dissolved in methylene chloride in the presence of tin(IV) chloride (for similar examples see ref. 16). Our inability to obtain the radical cation emission from pyrenealdehyde adsorbed to type Na<sup>+</sup>-Y zeolite and the reversibility of radical cation formation on the type Na<sup>+</sup>-Y zeolite mediated by atmospheric moisture are consistent with literature parallels [17, 18].

### 3. Conclusion

Pyrenealdehyde appears to be a sensitive probe of the interactions between aromatic compounds and zeolite binding sites. The observation of

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<sup>†</sup>See footnote to p. 202.

enhanced pyrenealdehyde excimer emission with adsorption, at very low surface coverage, to Na<sup>+</sup>-Y zeolite reflects the ability of the supercage cavity to orient the monomer units of molecular aggregates in a geometry conducive to excimer fluorescence. The zeolite cavities would be expected to be useful environments to mediate bimolecular cage reactions. We have, in fact, observed a dramatic increase in cage reactions for benzyl radicals sequestered within zeolite supercages compared with silica cages. (A cage effect of 100% is observed for asymmetric benzyl radical pair recombination with photolysis at room temperature of 1-(*p*-methylphenyl)-3-phenylpropan-2-one adsorbed to type Na<sup>+</sup>-Y zeolite [17]. the corresponding cage effect for the photolysis of the ketone to freeze-dried silica (surface area, 950 m<sup>2</sup> g<sup>-1</sup>; pore diameter, less than 20 Å) was 32% [17].

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