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Diffuse reflectance laser photolytic studies of naphthalene, biphenyl and some aromatic hydrocarbons adsorbed in the cavities of faujasitic zeolites

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Time-resolved absorption and emission characteristics of naphthalene, biphenyl and a few other aromatic molecules adsorbed in the cavities of zeolites NaX and NaY have been investigated as a function of sample loading. At low loadings, biphotonic ionization was observed to generate both the radical cations of guest aromatic species and trapped electrons in the zeolite frameworks. Different types of trapped electrons were found depending on the hydration levels of the zeolite, i.e. Na_4^{3+} in dehydrated zeolites and a mixture of Na_3^{2+} and Na_2^{+} in hydrated zeolites. As the loading was increased, increased formation of the radical anions of the guest species occurred with a significant decrease in the yield of trapped electrons. It was firmly established that radical anions are not produced from trapped electrons and neutral molecules on µs timescales. We propose, therefore, that they are produced from neutral molecules by scavenging photo-ejected electrons before they are trapped. This mechanism of anion formation is characteristic of zeolites in which acceptor molecules with restricted diffusional motions are concentrated in the vicinity of photo-ionized molecules in cage networks. The dimer cation of naphthalene was also found to be formed photochemically in the zeolite cage networks at high loadings. A specific effect of zeolite cages which facilitates the photochemical reactions of guest organic molecules is described.

Zeolites have attracted much attention in photochemistry.¹ They can host many organic guest molecules in their cavities or channels and such inclusions have often been shown to modify the normal solution photochemistry of a given species. For example, photoinduced electron-transfer reactions, for storage of solar energy, have been shown to proceed efficiently by impeding the back reaction, giving rise to long-lived charge separation.² Zeolites are crystalline aluminosilicates characterized by strictly regular structures.³ In particular, large-pore faujasitic zeolites (zeolites X and Y) consist basically of a 3D network of nearly spherical supercages of ca. 1.3 nm in diameter connected tetrahedrally through 0.74 nm windows. The supercages are primary sites for adsorbed guest molecules. It is suggested that small aromatic guest molecules such as benzene are adsorbed primarily at type II sites, interacting with some of the charge-compensating cations, viz. Na⁺ ions, and, secondarily, at 12-membered ring windows, interacting with the framework oxygen. These remarkable structural features of the zeolite cavities can provide new aspects of photophysical and photochemical processes of guest molecules.

Transient absorption studies of several aromatic molecules adsorbed into the cavities of zeolites have been carried out,⁴⁻¹⁰ and several unique aspects of the photophysics and photochemistry of these aromatic molecules, characteristic to zeolites, have been revealed; some controversial results have also been obtained. Thomas and co-workers⁴ observed the formation of the radical cations of aromatic molecules and trapped electrons in the form of Na_4^{3+} , which absorbs at 520 nm in NaY and 550 nm in NaX on laser excitation of pyrene, anthracene, naphthalene and trans-stilbene adsorbed in these zeolites. This shows that the photoionization of these guest molecules takes place as a primary event in the adsorbed state. On the other hand, Gessener and Scaiano⁵ failed to confirm the presence of Na_4^{3+} on laser photolysis of several aromatic molecules including naphthalene and trans-stilbene adsorbed in NaX, despite the fact that they detected the radical cations of these molecules. There still remain some uncertainties of the fate of photo-ejected electrons from guest

molecules in zeolite systems. We have initiated the present study to clarify this problem and gain comprehensive understanding of the general picture which may prevail for primary photoinitiated processes of aromatic molecules in zeolite systems.

Experimental

Naphthalene (Tokyo Kasei, zone refined), biphenyl (Tokyo Kasei, zone refined), anthracene (Merck, scintillation grade) were used as received. N-Methyl carbazole (Tokyo Kasei, >99%) and trans-stilbene (Tokyo Kasei, >98%) were recrystallized. n-Hexane (Wako chemicals, HPLC grade) was distilled and stored over 4A molecular sieves. Zeolite NaX (unit cell contents Na₈₅Al₈₅Si₁₀₇O₃₈₄ · xH₂O), zeolite NaY (unit cell contents $Na_{51}Al_{51}Si_{141}O_{384} \cdot xH_2O$) and zeolite USY (unit cell contents $Na_{0,4}Al_{0,4}Si_{191.6}O_{384} \cdot xH_2O$) were obtained from Tosoh Co., Japan. These three zeolites have the same crystal structure as faujasite and only differ in the ratio of Si to Al. Zeolite A (unit cell contents $Na_{12}Al_{12}Si_{12}O_{48} \cdot xH_2O$), which is crystallographically different from faujasite with a smaller cage, the α -cage, 1.1 nm in diameter with entry aperture of 0.4 nm, was also obtained from Tosoh. Silica gel was purchased from Merck (Silica gel 60, 230-400 mesh). These solid supports were calcined in air at 500 °C for 3-5 h just before sample preparation.

Samples were prepared by two methods: adsorption from the gas phase (method A) and adsorption from solution (method B). In method A, a weighed amount of calcined zeolite powder was placed in a cell attached to a vacuum line and evacuated at 0.1 Pa with heating up to 500 °C. Weighed amounts of aromatic guest molecules, placed in a container separated by a breakable seal from the sample cell, were also evacuated at 0.1 Pa, at temperatures between -5 and -70 °C. The sample cell was sealed and the seal was broken at room temperature. The cell was allowed to stand, either at room temperature or at 60-150 °C, for ca. 1 week until the adsorp-

J. Chem. Soc., Faraday Trans., 1996, 92(19), 3653-3660 3653 tion, by gas-phase diffusion, of guest organic molecules into the cavities of the zeolites was complete. The adsorption process was monitored by diffuse reflectance absorption and fluorescence spectroscopy of the guest aromatic molecules. Method A has the advantage of providing samples with the least adsorbed water contamination, although the sample preparation is time-consuming because of slow diffusion, and great care is necessary to prevent inhomogeneous distribution of guest molecules in the zeolites and the catalysed thermal decomposition of guest aromatics.

In method B, the samples were prepared by stirring dehydrated zeolite powder with n-hexane solutions of aromatic molecules in a stoppered vial under a nitrogen atmosphere at room temperature for 1-3 h; the sample was filtered, and the solid washed twice with n-hexane. The sample loading was calculated from the amount of aromatics remaining in the nhexane solution, determined spectrophotometrically. The guest loading levels ranged from 1×10^{-6} to 1×10^{-3} mol g^{-1} . Almost 100% adsorption was attained at these loading levels in NaX and NaY systems, i.e. the adsorbed molecules could scarcely be desorbed from NaX or NaY by washing with n-hexane, while a significant amount of molecules are desorbed from silica gel by the same treatment. We mostly failed to achieve adsorption on USY by method B, probably because of weak adsorption interaction in this system. The molecules used in the present study were scarcely adsorbable in NaA because their size is larger than that of the aperture. The samples were contained in 2 mm thick Suprasil cells and were evacuated at 0.1 Pa for 8 h at 0-5 °C. Evacuation at this temperature was intended to minimize the evaporation of guest aromatics but was found to result in incomplete removal of adsorbed water. Therefore, the evacuation of the samples was also carried out at 10⁻³ Pa at room temperature for nonvolatile aromatics, N-methyl carbazole and anthracene. Method B has the advantage of being carried out at room temperature and allows a relatively homogeneous distribution of guest molecules but the difficulty of removing contaminating solvents or water is a serious disadvantage.

The experimental setup for nanosecond diffuse reflectance laser photolysis, applicable to the detection of transient species in optically inhomogeneous and light-scattering systems, was similar to that described previously.¹⁰ A 266 or 355 nm beam from an Nd : YAG laser (Continuum NY61-10, 8 ns pulse width) was used for excitation. The output of the laser pulses was calibrated with a pyroelectric detector (Gentec ED-200). Transient absorption spectra were measured on an image-intensified multichannel photodiode array detector (Princeton Instruments IRY-512 G/R, 512 channels, gate width >5 ns) attached to a polychromator (Jobin-Yvon HR-320, 150 grooves mm⁻¹, blazed at 500 nm). A 60 W pulsed Xe flash lamp (EG&G FX-249, flat intensity for ca. 50 µs was used as monitoring light source. A typical experiment consisted of 20 replicate shots per measurement, and the average signal was processed with an NEC personal computer. The experiments were carried out with a 1 Hz duration and transients were confirmed to decay within 100 ms of excitation. In most cases, we used a wide gate width of 50 ns with long delays, in order to minimise disturbance by emission or reflected laser light. During laser experiments the samples were shaken after every 20 laser shots to ensure a fresh sample surface was presented, although no colouring due to the formation of permanent products was evident.

We adopted an approach by Wilkinson et al.¹¹ in which the percentage absorption is employed to describe the transient optical absorption signal following laser excitation of guest-doped zeolites.

absorption (%)(
$$\lambda$$
, t) = 100[1 - R(λ , t)/R₀(λ , t)]

where R and R_0 denote the intensities of the diffuse reflected light with and without excitation, respectively. The transient

absorption spectra were corrected for luminescence by subtracting a laser-only shot signal from the initial signal trace. Wilkinson's study¹¹ showed a linear relationship between the absorption and the amount of transient species present for absorption < 10%.

Femtosecond time-resolved transient absorption measurements were carried out by excitation with the second harmonics (390 nm, 170 fs pulse width, 210 μ J cm⁻² per pulse, 10 Hz) or the third harmonics (260 nm, 1.0 mJ cm⁻² per pulse) of a regenerative-amplified output of a Ti-sapphire laser (Coherent Mira 900 & Continuum TR 70). White continuum light was generated by focusing the fs fundamental (780 nm) into a quartz cell containing H₂O and used as a monitor light with various optical delays. The absorption signals were averaged 150 times.

Ground-state reflectance spectra were recorded with samples in 2 mm thick Suprasil cells on a Shimazu UV-3101PC double-monochromator spectrophotometer, equipped with an integrating sphere coated with $BaSO_4$. The reference was $BaSO_4$ (Kodak white reflectance standard). Fluorescence spectra were recorded on a Hitachi F-3010 spectrofluorimeter. Fluorescence lifetimes were measured on a Horiba NAES-1100 single-photon counting apparatus. The excitation source was a hydrogen discharge lamp.

All measurements were carried out at ambient temperature (19–21 $^{\circ}\mathrm{C}$).

Results and Discussion

Naphthalene in hydrated and dehydrated zeolite

Fig. 1(a) and (b) shows the transient absorption spectra of naphthalene (Nap) excited at 266 nm at various delays at two loading levels, 1.0×10^{-5} (a) and 5.0×10^{-4} mol g⁻¹ (b) adsorbed on NaY by method B. Note that the zeolite samples are inevitably hydrated owing to the method of preparation. Apart from an obvious T-T absorption band in the 400 nm region, spectrum (a) at 500 ns is assignable to the superposition of the bands of naphthalene radical cation (Nap⁺⁺) retaining vibrational structures and trapped electrons. The Nap⁺⁺ bands decay more slowly with peaks at 680, 660 and 630 nm, similar to the spectra reported previously for Nap^{*+}.¹²⁻¹⁴ The trapped electrons have a broad band peaking at ca. 750-800 nm. The assignment is based on the observation of a similar band on excitation of hydrated (20-30 wt.% water) NaY with a high intensity 266 nm laser light. Although this measurement was not carried out previously, it can reasonably be assumed that the direct excitation of a weak absorption band of NaY leads to photoionization and to generation of holes in the zeolite by release of electrons, which are eventually trapped in the zeolite framework. The transient spectra in hydrated NaY are similar with a band consisting of a mixture of Na₃²⁺ ($\lambda_{max} = 640-650$ nm) and Na_2^+ ($\lambda_{max} = 750-800$ nm) possibly formed in sodalite cages by trapping electrons on γ - or pulsed electron irradiation of dehydrated NaA.¹⁵ The similarity of the spectra supports our assignment. The trapped electrons are mostly generated by the photoionization of Nap, not from the NaY framework, because of the high absorptivity of Nap at the excitation wavelength. Trapped electrons were also observed with NaX doped with Nap, as will be shown below, but not with USY or silica gel. Only Nap'+ is observable on laser photolysis of these systems, suggesting the participation of Na⁺ for the observed trapped electrons.

Previous laser photolysis studies revealed the formation of Nap⁺⁺ in NaX. While Thomas *et al.*⁴ observed a broad band ascribable to Na₄³⁺ ($\lambda_{max} = 550$ nm) as a counterpart of Nap⁺⁺, Scaiano *et al.*⁵ failed to detect this species in NaX. We suggest that this difference is due to the different water contents of the zeolites used in these studies, although both



Fig. 1 Transient absorption spectra (10% per division) of Nap adsorbed from solution in zeolites at various delays ($\lambda_{ex} = 266$ nm): (a) 1.0×10^{-5} mol g⁻¹ Nap in NaY (13 mJ cm⁻²); (b) 5.0×10^{-4} mol g⁻¹ Nap in NaY (13 mJ cm⁻²); (c) 2.0×10^{-4} mol g⁻¹ Nap in NaX (16 mJ cm⁻²)

groups used the solution method for adsorption. We excited NaX with different water contents with a 266 nm laser pulse and observed two contrasting transient absorption spectra (see Fig. 2) both of which are assignable to different types of trapped electrons, on the basis of similarity of the spectra to those in the literature.¹⁵ At less than 2 wt.% water we observed a band due to Na4³⁺, while at 20 wt.% a band peaking at 750-800 nm, which may represent the superposition of the bands of Na_3^{2+} and Na_2^{+} , was observed. At intermediate water content (e.g. 10 wt.%), both of these bands of different decay rates were seen [Fig. 2(b)]. These results suggest that the number of sodium atoms comprising trapped electrons changes with increasing water content, from Na4³⁺ to Na_3^{2+} and Na_2^{+} . As a result, the peak position of their transient spectra changes with the water content in both NaX and NaY.

We measured the transient spectra of Nap adsorbed from the gas phase onto NaX and NaY. The spectra are similar to those reported by Thomas *et al.*⁴ and suggest that Na₄³⁺ is produced in dehydrated NaX and NaY. We also measured the transient spectra of Nap adsorbed from solution onto NaX. The result at a low loading level of Nap shows that trapped electrons different from Na₄³⁺ are formed in hydrated NaX.



Fig. 2 Transient absorption spectra (5% per division) of hydrated NaX at various delays ($\lambda_{ex} = 266 \text{ nm}$): (a) 2 wt.% water (106 mJ cm⁻²); (b) 10 wt.% water (72 mJ cm⁻²); (c) 20 wt.% hydrated (63 mJ cm⁻²)

Accordingly, we could show that the nature of the trapped electrons depends solely on the level of hydration of the host zeolite, regardless of the method of production.

The photoionization of Nap in zeolites appears to be a biphotonic process. We measured the transient absorption signal as a function of laser fluence (mJ cm⁻²) in the 600–800 nm region, due to Nap'+ and trapped electrons, and at 360-380 nm, due to T-T absorption of Nap in the hydrated systems at low loading levels of Nap. Despite the fact that the T-T absorption signal increases at low fluences and saturates at high fluences, the signal at the red wavelengths gave a concave curve. This behaviour is similar to that reported for photoionization of anthracene on a silica gel support,¹⁶ but markedly different from that reported for photoionization of anthracene and pyrene adsorbed on NaX and NaY zeolites.44 The ionization potential (E_i) of Nap (8.34 eV ¹⁷), higher than that of anthracene (7.41 eV¹⁷) or pyrene (7.41 eV¹⁷), is responsible for the difference in zeolites. We observed inefficient photoionization of Nap, which is also ascribable to a biphotonic process, in silica gel and USY systems. With regard to silica gel, the recognition that it provides a less polar environment to adsorbed molecules than zeolites with low Si/Al ratio (high Al content), is gaining popularity.¹⁸ USY has similar chemical composition to silica gel and is expected to provide a medium polarity, similar to silica gel.

Now, we consider the effect of the Nap loading level, neglected previously, since we expect, on the basis of our previous investigation, that the photochemistry of guest aromatic molecules is strongly dependent on their loading levels in zeolites. For example, at high loadings we observed excimer formation of anthracene^{10a} and photoinduced electron transfer of pyrene.^{10c}

At a high loading level in NaY, a significantly different transient spectrum from that at low loading [cf. Fig. 1(a) and (b)] is observed. The band due to Nap⁺⁺ has nearly disappeared

and a new broad band centred at 590 nm appears. In NaX at 2.0×10^{-4} mol g⁻¹ [Fig. 1(c)], the decrease in Nap⁺⁺ absorption and appearance of the 590 nm band is observed between 500 ns to 10 µs after excitation. This observation is characteristic of the NaX system. We regard this 590 nm band as evidence for the formation of Nap dimer cation, (Nap)2⁺, by comparison with that observed in y-irradiated lowtemperature organic glass,¹⁹ pulsed-electron irradiated solutions²⁰ and radiation- or photo-irradiated polymer solutions.²¹ This band is ascribable to a local transition of the dimer cation. Although the observation of charge resonance bands in the near-IR region is the most suitable for the assignment of dimer cations, we were unsuccessful in making transient absorption measurements in the near-IR region using our diffuse reflectance technique. We expect that Nap molecules are forced to be adsorbed at close distances in the limited space in the supercage networks at high loadings. On the basis of a molecular modelling calculation,²² we estimate that ca. 13% of the total volume of the supercage networks in faujasitic zeolites will be occupied by Nap molecules at a loading level of 5.0×10^{-4} mol g⁻¹ but only 0.27% at 1.0×10^{-5} mol g⁻¹. Although we cannot tell the relative orientation of these guest molecules in the supercages, fluorescence spectral changes dependent on Nap loadings suggest that an increasing number of guest molecules causes interaction at high loading levels. Fluorescence spectra, dependent on Nap loading, (method B) in NaY are given in Fig. 3, and suggest increasing formation of excimer with increasing loading. We rule out the possibility of dynamic excimer formation, known to occur in solution since (1) the excimer emission rises almost simultaneously with excitation pulse and (2) the decay of the monomer emission is unaffected by the loading. These results also suggest that aggregates, such as dimers of Nap, are formed in the adsorbed state. These aggregates are different from microcrystalline Nap since Nap shows no excimer emission in the crystalline state. Thus, $(Nap)_2^{+}$ is produced as a consequence of the excitation of these dimeric species formed in the ground state. The spectral change which occurred in NaX [Fig. 1(c)] may suggest a contribution from the dynamic formation of $(Nap)_2^{*+}$ from Nap^{*+} and Nap. However, the growth of the transient absorption signal at 590 nm was not observed to be at the expense of the decay of Nap⁺⁺, inconsistent with the assumption that the dynamic



Fig. 3 Steady-state fluorescence spectra (uncorrected) of Nap adsorbed from solution in NaY at various loading levels ($\lambda_{ex} = 280$ nm): (a) 1.0×10^{-5} ; (b) 1.0×10^{-4} ; (c) 3.0×10^{-4} and (d) 5.0×10^{-4} mol g⁻¹

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process is mainly involved in the dimer cation formation. The formation of dimer cations in zeolites by photoinduced processes has not been reported previously.

We now consider the fate of photo-ejected electrons in the system loaded with Nap in high concentrations. In Fig. 1(b), we notice a markedly slow decay in the 800-900 nm region compared with the band of trapped electrons in Fig. 1(a), indicating that the band is not due to trapped electrons. We assign this band to the anion radicals of Nap, Nap⁻⁻, because Nap⁻⁻ is known to absorb weakly with a peak at 820 nm.²³ As will be shown for other guest-loaded systems, anion radicals of guest molecules could be formed in zeolites at high loading levels.

Biphenyl in hydrated zeolite

Fig. 4 shows the transient absorption spectra ($\lambda_{ex} = 266$ nm) of biphenyl (Bip) adsorbed at three different loadings from solution onto NaY. An important observation at low loadings [see Fig. 4(a)] is a band peaking at 680 nm with a shoulder at 630 nm and a broad band in the 750-900 nm region. The former is reasonably assigned to the biphenyl radical cation (Bip⁺⁺) on the basis of published spectra^{12,13,24} and the latter, which decays faster, to the trapped electrons in zeolite, poss-ibly a mixture of Na_3^{2+} and Na_2^+ as in the case of Nap in hydrated NaY. Again, the trapped electrons are expected to be produced mainly by photoionization of Bip. The T-T absorption of Bip is known to lie in the region 360-370 nm and Bip⁺⁺ absorbs at 370-380 nm.¹² Thus, the absorption band below 400 nm is due to both these species. As in the Nap systems, photoionization to produce Bip⁺⁺ and trapped electrons is dominant at low loading levels. This photoioization is considered to take place by a biphotonic process because an upward curvature was obtained when the absorption at 680



Fig. 4 Transient absorption spectra (10% per division) of Bip adsorbed from solution in NaY at various delays [$\lambda_{ex} = 266 \text{ nm}$, 3.2 mJ cm⁻² ($\lambda > 450 \text{ nm}$) and 1.9 mJ cm⁻² ($\lambda < 450 \text{ nm}$)]: (a) 1.0 × 10⁻⁵; (b) 2.0 × 10⁻⁴ and (c) 1.0 × 10⁻³ mol g⁻¹

nm was plotted as a function of laser fluence applied. The E_i of Bip, 8.34 eV,¹⁷ is similar to that of Nap, which is ascribable to the cause of the biphotonic process.

On increasing the loading, the transient spectra change. At medium loading we observed a new peak arising at 620 nm and a decrease in the absorption band at >750 nm. The band at 620 nm can be assigned to the biphenyl radical anion (Bip^{*-}) .^{12,13,24} Further increase in the Bip loading gives a clearly diminished band due to trapped electrons with concomitant increase in the Bip^{*-} band. An ill-resolved band at 400 nm may also be an indication of Bip^{*-}.¹² A range of values for molar absorptivity (ε) of Bip^{*+} and Bip^{*-} has been reported^{12,13,23a,24} with rather larger values for Bip^{*+}.

The radical anion can be formed by intercepting photoejected electrons before they are trapped in the framework zeolite. This explanation is based on the fact that the only spectral change observed after excitation is the decay of bands of individual species with no indication of interchange such as from trapped electrons to anion radicals or vice versa. There is also no indication of formation of trapped electrons or Bip' by electron transfer from zeolites, *i.e.* the formation of Bip^{*+} is coupled with the observation of Bip^{*-}. Trapped electron formation or anion formation seems immediate on our timescale: the transient spectrum produced at zero delay time decays with time without any major spectral change, regardless of loading. If the mechanism of radical anion formation in the Bip/NaY system is described as trapping of photo-ejected electrons produced on excitation of Bip before they are trapped by host zeolite, the maximum ratio of Bip⁻⁻ to Bip⁻⁺ is expected to be unity. This seems to occur in the Bip/NaY system at high loadings. Although quantitative determination of the ratio of anion to cation radicals is difficult at present, because of uncertainty of ε for these species and insufficient separation of the bands, the qualitative picture of Bip⁻⁻ formation is in accord with the experimental results. Note that we observed a similar transient absorption spectrum assignable to Bip⁺⁺ for Bip adsorbed on silica gel at two different loadings, suggesting that Bip^{•-} is not formed on this support.

Further support for this mechanism of Bip⁻⁻ formation comes from the measurement of fluorescence lifetime of Bip in NaY. The fluorescence spectra of Bip in NaY is similar to that of monomer emission with less perceptible vibrational structures than that in solution at loadings less than 2.5×10^{-4} mol g⁻¹ while a small tail is noticeable at 1.0×10^{-3} mol g⁻¹. Thus, intermolecular interaction of Bip is increasingly evident at high loading. In spite of the spectral change, the fluorescence decay rate of monomer emission is unaffected by loading. This suggests that the fluorescent state of Bip is free from concentration quenching. Consequently, the contribution from a pathway via an excited state electron transfer to give Bip^{•-} is negligible. The pick-up of photo-ejected electrons from Bip by nearby Bip molecules is most plausible. We observed a similar transient spectral change with loading in Bip/NaX systems.

Anthracene in dehydrated zeolite

We now consider the effect of guest loading levels in dehydrated zeolite systems using anthracene adsorbed from the gas phase into NaX. Anthracene was excited at 355 nm, where the absorption of the excitation beam by the host zeolite is negligible. Fig. 5 shows the transient absorption spectra at two typical loadings. Note that the ground state of anthracene scarcely absorbs at wavelengths longer than 400 nm under the present experimental conditions. By comparison with Nap and Bip, we assume that the main observation at the low loading is photoionization to produce anthracene radical cation(Ant⁺⁺) whose absorption peak is located at 715 nm^{12,13,16,25} and trapped electrons in the form of Na4³⁺ with



Fig. 5 Transient absorption spectra (5% per division) of Ant in dehydrated NaX at various delays ($\lambda_{ex} = 355 \text{ nm}$): (a) $5.0 \times 10^{-6} \text{ mol g}^{-1}$ (15 mJ cm⁻²); (b) $5.0 \times 10^{-4} \text{ mol g}^{-1}$ (12 mJ cm⁻²)

a broad band centred at 550 nm in NaX. The slow decay rate of the trapped electrons appears similar to that of Ant^{*+}, which suggest that recombination of these species is mainly responsible for the decay in dehydrated systems. This observation is in marked contrast with hydrated systems where the decay of trapped electrons is faster.

With increasing loading the relative intensity of the 550 nm band to the other band decreased. The band in the red becomes slightly broader and its peak wavelength shifts slightly to 720 nm. Note that the excimer emission of anthracene contributes more significantly at increasing loading at the expense of monomer emission; this observation suggests that the guest molecules are sufficiently close together to cause intermolecular interaction, similar to the Nap and Bip systems. First we assumed that the transient spectral change at high loadings is explained by the interception of photoejected electrons from Ant* by nearby Ant molecules before the electrons can be trapped by zeolite to form Na_4^{3+} . We tried to observe this process with a femtosecond absorption measurement ($\lambda_{ex} = 390$ nm) and observed a slow increase in the absorption signal in the red band ranging from 50 to 200 ps in addition to a fast increase within 30 ps after excitation at 5.0×10^{-4} mol g⁻¹ loading, however, we failed to observe a change in the absorption at 550 nm because of strong excimer emission. At present, we assume that the trapping of photoelectrons is extremely fast and the observed slow growth is due to electron transfer: Ant* + Ant \rightarrow Ant* + Ant* -, indicated by concentration quenching of Ant monomer fluorescence: faster decay rates of Ant monomer fluorescence were observed at higher loadings, and the two processes may contribute to the observation at high loadings. The probability of interception of electrons is governed by the number of Ant in the vicinity of the excited guest molecules. Ant⁻ is reported^{12,13,25} to absorb at similar wavelengths ($\lambda_{max} = 725$ nm) to that of Ant⁺⁺ in solution and it is difficult to resolve

the spectral region in Fig. 5. Although we are not able to show definite evidence that Ant^{-} is present, our explanation for the mechanism of Ant^{-} formation is consistent with that of Bip⁻ formation in hydrated NaY. The widely used scavenging reagents, oxygen for anion radicals and amines for cation radicals, for solution studies proved ineffective or caused damage to our zeolite samples, and were not used in this study. The dehydrated zeolite systems loaded with guest molecules give rise to reaction processes similar to those in hydrated systems on photo-excitation of guest molecules as far as photo-ejected electrons are concerned. Samples of anthracene/NaX prepared by method B followed by evacuation at 10^{-3} Pa at room temperature gave similar transient spectra to those prepared by method A.

Other systems: trans-stilbene and N-methyl carbazole

We measured the concentration-dependent transient absorption spectra, excited at 266 nm, of trans-stilbene (T-St) in NaY and N-methyl carbazole (MeCA) in NaX, both prepared by method B. The T-St/NaY samples were evacuated at 0.1 Pa at 0-5 °C while MeCA/NaX samples were evacuated at 10^{-3} Pa at room temperature. A similar reaction occurred to that with the other guest molecules. Assuming a similar absorption spectrum for MeCA⁺⁺ to that of N-ethyl carbazole radical cation (EtCA⁺⁺), we observed the cation radicals of guest molecules $[\lambda_{max}(T-St^{*+}) = 475 \text{ nm}^{26} \text{ and } \lambda_{max}(EtCA^{*+}) = 780$ nm²⁷] together with trapped electrons at low loading levels. The types of trapped electrons were different, *i.e.* Na_3^{2+} and Na₂⁺ in the T-St/NaY system and Na₄³⁺ in the MeCA/NaX system. At high loading, the observed spectra are due to superposition of the band of radical anions on that of the radical cations. The broader bands at early times are an indication of the formation of T-St⁻⁻ at high loadings, since this species absorbs at *ca.* 500 nm.²⁶ A sharp band at 395 nm, indicative of MeCA^{-,27} is observed for MeCA in NaX. This band is only observed at high loadings and is distinguished from the T-T absorption band which occurs at 420 nm.²⁷ Thus, in zeolites NaX and NaY systems, we observed more or less similar photochemical processes of the organic adsorbates on the timescale of $<1 \,\mu s$. These processes are difficult to observe by our transient spectroscopic method for other systems, such as silica gel.

Laser photolytic generation of trapped electrons in zeolites

Trapped electrons in various forms of sodium ion clusters have been generated in dehydrated zeolites by reduction with alkali-metal vapour,²⁸ lithium and organolithium reagents in solution²⁹ and by γ - and pulsed electron-irradiation^{15,30} and were found to be stable at room temperature. In addition, Thomas *et al.*³¹ recently reported the production of trapped electrons in dehydrated zeolites by irradiation with far-UV light (185 nm from a low-pressure mercury lamp and 195 nm from an ArF excimer laser). We also found the formation of trapped electrons in dehydrated zeolites on excitation of their absorption band edge with high intensity nanosecond laser light of 248 nm (KrF excimer laser) or 266 nm.³²

As shown in Fig. 2 for NaX, the spectra change with different levels of hydration of zeolite. It was suggested³³ that water molecules which penetrate inside small sodalite cages and supercages dissolve the counter ions of negatively charged Al, *i.e.* Na⁺ into their clusters or pools. Accordingly, the number of Na⁺ attached to Al in the frameworks of zeolite and, thus available for formation of sodium ion clusters, decreases with increasing water content. This assumption was confirmed³⁴ by the measurement of ²³Na NMR linewidth for the transition between m = +1/2 and -1/2 in NaX with different water content. The linewidth decreased with increasing water content between 0 and 30%. This result is in accord with a model in which the movement of Na^+ is enhanced at high water content.

Our assignment of the transient absorption spectra to sodium ion clusters $(Na_n^{(n-1)+})$ is based on the work by Thomas *et al.*¹⁵ who compared the absorption spectra of these species in various types of dehydrated zeolites with their EPR spectra which identify the number of Na atoms participating in cluster formation by observation of the number of finestructure lines. We assigned the red band of trapped electrons in hydrated zeolites to a mixture of Na_3^{2+} and Na_2^+ since the bands observed seem too broad for a single species and the peak wavelength shifted with the water content. This assignment involves some uncertainty. However, the short lifetimes of trapped electrons meant that we could not measure EPS spectra in hydrated zeolite systems.

The decay kinetics of the trapped electrons in zeolites deviate from an exponential function and the decay rate is dependent on their water content. For less than 2 wt.% water content $(1.1 \times 10^{-3} \text{ mol g}^{-1})$ in NaX, the spectra are similar and assignable to Na₄³⁺; however, the decay rate becomes fast for higher water content. On the other hand, the band of trapped electrons in the red which is observed at high water content and assigned to the mixture of Na₃²⁺ and Na₂⁺, decayed without a simple correlation with the water content. The decay of this band in the presence of guest aromatics seems faster and is not correlated with the decay of cation radicals of guest aromatics. This may be due partly to the sample preparation method (method B) which is inefficient for removal of reactive impurities such as oxygen, water and *n*-hexane adsorbed in zeolites.

Zeolites as a medium for photochemical reactions

Zeolite pores³⁵ are akin to solvent cages despite their rigid framework structures. The pores and cages provide medium polarities dependent, for example, upon the Si/Al ratio. They also provide acid-base properties and hydrogen-bonding abilities. In particular, zeolites NaX and NaY with high Al contents are known to afford a polar environment¹⁸ and it is pertinent to compare photochemical reactions in these systems with those in polar solvents and silica gel systems.

Our mechanism for the photoinduced radical anion formation in our zeolite systems is that the photo-ejected electrons generated on excitation of guest aromatics are scavenged before they are trapped by the zeolite framework. Once they are trapped in the zeolite framework they become unreactive toward guest aromatics in less than µs. This mechanism seems ubiquitous but does not apply to solution systems. Small quantum yields and fast decay channels inherent to photochemical processes in solution systems hampered the observation of radical anion formation. For example, Delcourt and Rossi³⁶ attempted the nanosecond 249 nm laser photolysis of several unsaturated hydrocarbons including naphthalene, trans-stilbene and fluorene (an analogue of biphenyl) in acetonitrile. The only firm evidence obtained is for the formation of radical cations by photoionization. Although they suggested the formation of anion radicals and of dimer cations in their reaction scheme, they failed to observe these species. In this case, photo-ejected electrons are expected to form either solvated electrons or solvent anion radicals, and these species would then react with solute hydrocarbons. However, the cations and electrons produced recombine well before the formation of anion radicals. The difference between solution systems and zeolites is due to the mobility of solvent molecules and solvent anions. In addition, the electron affinity of zeolite is lower than that of acetonitrile, although estimation of its value is difficult. Thus, the higher reactivity of solvent towards photo-ejected electrons is the primary cause of inefficient anion radical formation in solution. This idea also

applies to the silica gel system, where neither trapped electrons nor anion radicals of guest molecules were observed. Silica gel seems more reactive towards photo-ejected electrons: some impurities or defects may 'wipe out' photoejected electrons. The second feature of zeolite is to give guest molecules a chance of accepting photo-ejected electrons by creating a high local concentration and retarding the recombination of radical anions with radical cations by holding molecules in the cage networks and restricting their diffusional motions.

The formation of anion radicals is common in radiation chemistry where more efficient production of electrons is possible by γ - or pulsed electron-irradiation of the host materials. It was established^{13,20b,24a,37} that solvated electrons or solvent anions initially produced react to form solute anion radicals in many solution systems. A few studies³⁸ also reported the formation of radical anions in γ -irradiated silica gel doped with aromatics, despite some erroneous assignment of the cation radicals of biphenyl and naphthalene to their anion radicals in early studies.^{38a} Nevertheless, if we apply this idea of generating anion radicals to zeolite systems, we notice that the situation is completely different. Direct excitation of zeolite, either by radiation or UV-photons, produces trapped electrons which are unreactive toward guest molecules since they are considered to be formed inside the sodalite cages which are inaccessible to the guest molecules. In order to react, the guest molecules must be able to scavenge mobile electrons before they are trapped in the zeolite frame.

Photoinduced electron transfer reactions are responsible for formation of anion radicals in polar media. Only a few cases of electron transfer between excited and ground-state molecules have been reported in solvents such as acetonitrile. For example, perylene(Pe) in solution was reported³⁹ to produce radical anions and radical cations of Pe. We have reported^{10c} recently that photoinduced electron transfer takes place for pyrene (Py) adsorbed in NaX and NaY zeolites. Our conclusion is based on the formation of increasing amounts of radical anions, Py⁻⁻ with increasing loading of Py on photoexcitation together with the observation of concentrationdependent fluorescence quenching. In the present study, no evidence was obtained for electron transfer to form anions except for anthracene systems, where quenching of fluorescence occurred concomitantly with formation of radical ions^{10a} on a picosecond timescale. Electron affinities are a good measure for predicting the occurrence of electron transfer of this type although the geometry specific to adsorbed molecules seems also to be important in zeolite systems. We have evidence⁴⁰ that excitation of strong electron acceptors such as 1,2,4,5-tetracyanobenzene (TCNB) adsorbed in NaY gives rise to anion radicals. This is explained by electron transfer to the excited state of TCNB from zeolites and shows the importance of electron affinity for photoinduced electron transfer reactions of guest molecules. In the present study, we mostly observed the formation of radical anions via trapping of photoelectrons for guest aromatics with intermediate electron affinities.

Summary

The present study has shown that the photoreactions of guest aromatics in zeolites are dependent both on chemical properties and the loading of the guest molecules. At low loadings, radical cations are produced as a result of biphotonic photoionization of guest molecules with $E_i > 8$ eV. It has been shown^{4a} that guest molecules with E_i as low as 7.5 eV are ionized from the S₁ excited state through monophotonic process in zeolites. The counterpart of the radical cations were suggested by others⁴ to be trapped electrons produced in zeolite skeletons, but we have shown for the first time the different behaviour of trapped electrons, dependent on the hydration of the host zeolites. These trapped electrons are unreactive toward guest aromatics once formed in the zeolite frameworks because of limited accessibility to the guest molecules. At high loadings, the formation of anion radicals was observed and the mechanism is ascribed to scavenging of photo-ejected electrons, a precursor of trapped electrons. This mechanism seems to prevail in zeolite systems although a photoinduced electron trasfer mechanism is possible in certain cases.^{10c} Note that the present observation of long-lived anion radicals together with long-lived trapped electrons is characteristic of zeolites, and is not obtainable in other solid supports such as silica gel. Dimer cation formation is also characteristic of zeolite systems; dimer cations are formed depending on the loading level of the guest species. Since molecular association in supercage networks is extensively observed at high loadings, dimer cations can be formed photochemically for many other guest aromatic molecules besides naphthalene.

The results obtained in the present study are in accord with our previous notion of molecular tethering in zeolites¹⁰ *i.e.* the confinement of more than one molecule within a tight space of supercages creates a situation which is akin to that of molecules connected with a chemical bond. The formation of dimer cations and cation-anion pairs in supercage networks is a result of molecular tethering.

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