Review

Zeolite photochemistry: impact of zeolites on photochemistry and feedback from photochemistry to zeolite science

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Received 23 September 2002; received in revised form 3 February 2003; accepted 3 February 2003

Abstract

The past decade has witnessed increasing activity in photochemistry within zeolites. This article critically reviews the topics of such activities and provides some comments for future studies. Particular emphasis is placed on transient spectroscopic studies, which have shown to be a powerful technique for mechanistic investigations in solid systems. As a host material for organic species, zeolites are another promising candidate for modifying the photophysics and photochemistry of a given species. Besides, photochemical reactions can be pursued in zeolites and provide product distributions considerably different from those in solutions. Accordingly, photochemistry has enjoyed a great benefit from zeolite materials and zeolite science. In return, photochemical techniques can provide pieces of useful information on the fundamental issues of zeolite science such as adsorption and diffusion of molecules within the zeolite. Thus, we can expect further development in this area if this cooperative relationship continues. In this article, we mainly describe mechanistic aspect of photochemical reactions. Issues associated with experimental techniques are also reviewed.

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Keywords: Zeolite; Photochemistry; Adsorption; Diffusion; Transient

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1. Introduction

Zeolites have been an object of scientific research and a material beneficial to mankind for more than 200 years since their discovery in 1756. However, it was not until 10–15 years ago that zeolites attracted the keen interest of photochemists who wanted to use them for their research. Since then, an active interplay of zeolites with photochemistry has started [1–11]. Photochemists are most interested in controlling chemical reactions with the aid of zeolites and other supramolecular assemblies, aimed at constructing artificial photosynthetic systems, controlling chirality and inventing nanoscale advanced materials. Zeolites are found to be particularly useful for such purposes since they host various molecules including organics in their cavities and channels, and such inclusions have often been shown to modify the normal solution photochemistry of a given species. The confinement of molecules within the constrained space and the catalytic activity of the surface adsorption sites were considered decisive for product distributions unique to zeolites. On the other hand, zeolite science covers a broad spectrum, from synthesis to structural characterization, adsorption and transport phenomena, and applications such as catalysts and other classical uses (adsorbents or desiccants, water softeners, soil improvers, and so forth) [12–14]. Furthermore, zeolites have been recognized as new materials for optical and electronic applications, such as lasers, quantum dots and second harmonic generation, in recent years [15–18]. These days, zeolite science as materials science is getting closer and closer to photochemistry than ever before.

Despite their high interest and anticipation, many photochemists who have worked in the gas phase, in transparent solutions including micelles and colloids, and on single crystals are still skeptical about zeolites and hesitate to utilize them for their research mainly because of distrust of the reliability of the systems as well as that of the spectroscopies to deal with them. The following questions are frequently asked. How much are we sure about the postulate that the location of adsorbed molecules is inside the cages and channels of zeolites? Can you obtain a homogeneous distribution of guest molecules among the cavities rather than a heterogeneous one? Are the transient absorption spectra obtained by a diffuse reflectance technique reliable enough? Zeolites are, of course, not an ideal system perfectly suited for controlling chemical reactions; rather, they bear some drawbacks, but we believe there are some ways to utilize them to their maximum capability for our purposes if we are fully aware of their physical and chemical properties. Along this line, we try to relieve the uneasiness brought about from the skepticism of many photochemists by carefully examining the experiments carried out with great efforts to show that zeolites are certainly usable even for sophisticated research.

This article critically reviews the photochemical studies within zeolites and summarizes the progress made during the past 10 years with the goal of providing useful information to photochemists regarding the advantages and limitations of zeolites for photochemical use. Particular emphasis is placed on the mechanistic studies where the transient absorption spectroscopic method, the most powerful way to look at reaction mechanisms, is employed, and the current understanding to the field will be presented. Additionally, consideration is given to issues to overcome in the near future. Although a number of review articles dealing with photochemical studies in zeolites have been published in the past few years [1–11], most articles cover rather specific subjects such as organic photochemistry, charge transfer (CT), confinement, the antenna effect, radical reactions, etc. We try to organize diverse subjects relevant to zeolites from the mechanistic point of view revealed by using the transient spectroscopy.

2. Materials, property and methodology

2.1. Structure and chemical properties of zeolites

Zeolites are microporous crystalline aluminosilicate materials, with alkali or alkaline earth metals as counterions [12–14]. As pictorially represented in Fig. 1, they consist of a framework of \([\text{SiO}_2]^\text{4-}\) and \([\text{AlO}_2]^\text{5-}\) tetrahedra, linked to each other at the corners by sharing their oxygens. This leads to the following general formula:

\[
(M^+)_x[\text{AlO}_2]^y\text{SiO}_2]_z \cdot m\text{H}_2\text{O}
\]

![Fig. 1. Framework structure of sodalite-based zeolites.](image)
In this formula, M\(^+\) represents the alkali metal cation. The tetrahedra make up three-dimensional network structures to form channels and cages or cavities of discrete size.

In aluminum-containing zeolites, negative charges generated in the framework originating from the difference in charge between the \([\text{SiO}_4]^{4-}\) and \([\text{AlO}_4]^{5-}\) tetrahedra must be balanced by the charge-compensating cations. These cations can generally be exchanged by conventional methods of ion exchange. The cations and water molecules present are located in the cages (cavities) and channels. Several types of zeolites are frequently employed in photochemical research: their common names are X, Y, A, mordenite, L, ZSM-5, silicalite, MCM-41, to name a few. In the crystallographical classification [19], X and Y belong to FAU (faujasite), A to LTA, L to LTL, and ZSM-5 and silicalite to MFI. These three-letter framework type codes were assigned by the Structure Commission of the International Zeolite Association (http://www.iza-structure.org/).

The chemical composition of zeolites is not necessarily limited to the aluminosilicate: aluminophosphate-based zeolites with the AlPO\(_4\) lattice and molecular sieves composed of other elements have been synthesized and exhibited catalytic properties distinct from those of aluminosilicate-based zeolites [14].

The structure of faujasite zeolites (zeolites X and Y) is cubic and built from sodalite cages (\(\text{H}_{9251}\)-cages, 0.66 nm in diameter, with an entry aperture of 0.21 nm) connected via the double 6-membered ring (D6R) frame. Note that the entry aperture of the sodalite cage is too small for the oxygen molecule to enter; however, water molecules are known to go in. Zeolites X and Y have different framework Si/Al ratios: 1.0 < Si/Al < 1.5 for zeolite X and 1.5 < Si/Al < 3 for zeolite Y. Interestingly, no faujasite with Si/Al ratio of less than 1.0 has been prepared to date because of the unstable framework structure (Loewenstein’s rule [20]). These zeolites form a three-dimensional network of nearly spherical supercages of about 1.3 nm in diameter connected tetrahedrally through 0.74 nm windows (diamond lattice). The supercage concentration in zeolite Y, with Na\(^+\) ions as the charge-compensating cation (Na\(^+\)-Y), is estimated to be approximately \(6 \times 10^{-4}\) mol/g on the basis of the crystal structure. The charge-compensating cations are mobile and distributed among several types of sites: S\(_I\) (both in X and Y) in the center of the D6R cage, S\(_J\) (both in X and Y) inside the sodalite cage, S\(_K\) (both in X and Y) on top of the hexagonal faces of the sodalite cages facing into the supercage and S\(_M\) (only in X) on the four-rings on the supercage wall. Only cations at S\(_K\) and S\(_M\) are accessible to the organic molecules adsorbed within a supercage. A de-aluminated zeolite [21,22] can be prepared through various post-synthesis modifications. Ultra-stable zeolite Y (USY), for example, de-aluminated by hydrothermal treatment and subsequent extraction of the extra-framework aluminum, has fewer charge-neutralizing cations, resulting from the decrease in the aluminum content and consequently provides less polar environment in supercage networks than Al-containing zeolites do.

Zeolite A is a synthetic material, the structure of which is also composed of sodalite cages similar to faujasite but connected through double 4-membered ring (D4R) of \([\text{SiO}_4]^{4-}\) and \([\text{AlO}_4]^{5-}\). By this connection, three cages are present: D4R, sodalite cage, and \(\alpha\)-cage (1.1 nm in diameter with a 0.41 nm opening). The structure of zeolite A is also cubic, having a Si/Al ratio of 1.0, with alternating Si and Al atoms in the framework. Aromatic guest species are hardly adsorbed inside the \(\alpha\)-cage because of size restrictions, and only external surfaces are available for the adsorption of small quantities.

Pentasil (5-membered ring) units as building blocks, in contrast to the sodalites, constitute channel-type zeolites such as ZSM-5 and mordenite. ZSM-5 and its high-silica analogue silicalite possess a structure consisting of two intersecting channel systems, with the vertical channel being elliptical (0.57 mm × 0.51 nm), whereas the horizontal channels have nearly circular 0.54 nm × 0.56 nm openings. On the other hand, the channel system in mordenite is a one-dimensional 12-membered ring system with an opening of 0.65 nm × 0.70 nm. Of other channel-type zeolites, zeolite L has a unidimensional channel system as in the mordenite, formed by 6- and 4-membered rings (Fig. 2).

![Fig. 2. Framework structure of zeolite L.](image-url)
The main channels of zeolite L are made by the stacking of sections with a length of 0.75 nm in the c-direction. The sections are joined by shared 12-membered ring windows having a free diameter of 0.71 nm. These rings make up the narrowest parts of the main channel. The largest free diameter is about 1.3 nm and lies midway between the 12-membered rings. In zeolite L, five positions are found for the extra-framework cations, i.e. sites A, B, C, D and E. Only the cations in site D are exchangeable at room temperature. Additionally, the synthesis of mesoporous (extra-large-pore) channel-type aluminosilicates, which allow the inclusion of molecules larger than that possible with faujasite zeolites, has been reported recently [23]. The crystalline aluminosilicate MCM-41 is formed from an array of parallel hexagonal channels whose diameter can be controlled from 2.0 to 6.0 nm by varying a template during its synthesis. These zeolites present an interesting contrast in topology, as well as in the sizes of pores or channels and of their openings from an entrapment point of view—adsorbing molecules inside the zeolites in a size-selective, shape-selective manner.

Zeolite can be regarded as a solvent that dissolves or disperses molecules into pores and channels, similar to solvent cages [4]. The solvation-like interaction can be expected for zeolite host–guest molecule pairs, and the negatively charged framework, and the mobile cations combine to produce an electrostatic field akin to solvent polarity inside the cavities where the molecules reside. The electrostatic field strength (polarity) in zeolites has been suggested to be extremely high [24–26] and is considered to be due to the fact that the cations exposed at the center of the supercage being only partially shielded. The electric field strength is dependent both on cation size and on Si/Al ratio. For example, the small Li\(^{+}\) ion induces a stronger field in its proximity than the larger Cs\(^{+}\) ion. Also, cations in zeolite Y exhibit higher fields than those in zeolite X. The effects of the fields, being akin to those of solvent polarity, have been explored with a number of fluorescence probes incorporated into zeolites [27–31]. Despite the similarity of zeolite pores to solvent shells, zeolite pores are rigid and distinctly shaped, in contrast to the soft and featureless solvent shells. Examination of physical and chemical properties characteristic to the zeolite is appropriate to gain some insight into the active role of the host material. Zeolites have amphoteric properties, and the existence of acid and base sites is well documented [32–37]. The bridging Si-OH···Al group is usually referred to as a Brønsted acid site in zeolites. On the contrary, no basic framework OH group has been reported to exist. Zeolites contain Lewis as well as Brønsted acid sites. The three-coordinated aluminum sites on the framework and non-framework Al sites are normally considered to be Lewis sites.

Additionally, charge-compensating cations act as Lewis acids, while the framework oxygens represent a base. In particular, the oxygens adjacent to Al (Si–O–Al oxygens) are more basic because of a larger negative charge on oxygen. The Lewis acidity is usually connected to an electron-accepting property, and the basicity to an electron-donating property. Thus, the zeolites behave both as electron donors and as acceptors of moderate strength to the guest species, depending on the adsorption site. As a rule, the acid strength or the electron-accepting ability increases with increasing Si/Al ratio and for zeolites with smaller alkali metal cations. For example, Li\(^{+}\)-Y is more acidic than Cs\(^{+}\)-X. On the other hand, the basic strength (electron-donating ability) of the zeolites increases with decreasing Si/Al ratio and for zeolites with larger alkali metal cations. In this regard, Cs\(^{+}\)-X is more basic than Li\(^{+}\)-Y. Accordingly, the chemical properties of the zeolites can be fine-tuned in terms of composition, cations and framework structure. The resulting properties can be assessed on the basis of Sanderson’s electronegativity: the electronegativity of the zeolites calculated according to the Sanderson’s equalization principle [38] has been used as a good measure of the electron-accepting ability of zeolites. Likewise, Sandarson’s partial charges of the framework oxygen atoms serve as viable measures of the framework donor strengths [39]. More recently, an alternative computational approach to the basicity of framework oxygens has been developed based on quantum chemical calculations [40].

The remarkable structural features and physicochemical properties of zeolites are expected to provide new aspects of photophysical and photochemical processes that can be monitored by employing transient spectroscopy and other techniques.
2.2 Adsorption

Adsorption is one of the fundamental issues in zeolite science [12–14]. Fig. 3 represents an adsorption isotherm of N$_2$ in zeolite Na$^+$-Y (Tosoh Lot. #3001) at 77 K measured in our laboratory. As is clear from the figure, adsorption of N$_2$, which is easily incorporated into the supercages, occurs in two stages with increasing equilibrium pressure. The initial, very steeply rising part implies that N$_2$ is being adsorbed into the supercages, and the following flat part, where the adsorption takes place very slowly with increasing pressure, accounts for N$_2$ molecules covering the outer surfaces of the zeolite at a monolayer level. In this case, more than 90% of the N$_2$ molecules were adsorbed in the supercages. This curve gives a basic idea of why zeolite scientists think a priori that adsorption takes place mostly in the supercages and that the molecules first go into the supercages. A simple explanation for the result is that most of the molecules are adsorbed into the supercages, because the volume of the supercages dominates, and the adsorption takes place first in the cages mainly because of a big gain in entropy.

Size exclusion is a basic guideline for adsorption of molecules in zeolites. Here, we give a nice example of the size exclusion in zeolites. The maximum quantities that could be adsorbed in Na$^+$-X zeolite from $n$-hexane solution at 296 K were compared for anthracene and the anthracene derivatives, 9-methylanthracene (MA), 9,10-dimethylanthracene (DMA) and 9,10-diphenylanthracene (DPA) [41].

\[
\begin{align*}
\text{anthracene} & \quad (5.3 \times 10^{-7} \text{ mol/g}) \\
9\text{-methylanthracene} & \quad (3.2 \times 10^{-7} \text{ mol/g}) \\
9,10\text{-dimethylanthracene} & \quad (5 \times 10^{-7} \text{ mol/g}) \\
9,10\text{-diphenylanthracene} & \quad (1 \times 10^{-7} \text{ mol/g})
\end{align*}
\]

The results are shown in the parentheses: anthracene was adsorbed to the extent of nearly one molecule/cage, and the slightly larger MA was adsorbed to an extent slightly less than that of anthracene. However, an abrupt decrease in adsorbed quantity was observed for DMA and DPA both of which apparently have a size larger than the aperture of the supercage in the Na$^+$-X zeolite. Thus, the adsorbed amounts of DMA and DPA may represent the molecules located on the outer surfaces of the zeolite. The measurement of the maximum quantity adsorbed can give an idea about the location of molecules, i.e. whether inside or outside. Note that the maximum amount of anthracene adsorbed on Na$^+$-A zeolite is well less than $1 \times 10^{-6}$ mol/g. Another example is a CT complex of arene donors formed in methylviologen (MV$^{2+}$) exchanged zeolites. Yoon et al. found that the appearance of the CT absorption bands strongly depend on the molecular dimensions of arene donors and they concluded that the complexes form inside the cages and channels in a size-selective, shape-selective manner [42–45]. These two cases show that adsorbed organic molecules reside mainly inside the zeolites if they can meet the requirement of size limitation imposed by the entry apertures to the cages.

As mentioned in the case of N$_2$, the process of adsorption is a dynamic one involving diffusion of adsorbates. A pictorial representation of this process is given by fluorescence spectroscopy [46]. A fixed quantity of anthracene (1.3 $\times$ 10$^{-4}$ mol/g) was adsorbed on Na$^+$-Y zeolite by sublimation at 150°C for 27 h in an evacuated container, followed by the measurement of the emission spectra of the samples with time. In one experiment, a sample was left at room temperature, while in the other case, another sample was kept in a drying oven at 150°C. Fig. 4 compares the emission spectra of these samples.

Initially, a broad and structureless band centered at 500 nm ascribable to the excimer emission is dominant, in addition to a structured band assignable to the monomer emission.
When kept at 150 °C, the contribution of the excimer emission decreased appreciably (B), indicating that the anthracene molecules initially accumulated on the external surfaces of the zeolite particles, thus giving rise to excimer emission, diffused into the particles, resulting in the monomer emission. On the other hand, when kept at room temperature, the reduction in the contribution of the excimer emission took place, but only very slowly (C), suggesting that the diffusion of anthracene molecules from the exterior surface to the interior of the particles is a very slow process at room temperature. Accordingly, the fluorescence spectroscopic method demonstrates nicely that it can indicate the location of adsorbed molecules on zeolites and also trace their diffusional motions from outside to inside the zeolite crystal driven by the concentration gradient.

Adsorption on the external surfaces of zeolites was examined by Turro’s group using aromatic ketones such as dibenzylketones (DBKs) which have a larger affinity for the surface than plain aromatics because of the polar –C=O group [47,48]. MFI zeolite was employed, whose channel aperture has a smaller size than these molecules, such that they cannot enter the channels. Under these circumstances, the adsorption isotherm was measured, and analysis based on the Langmuir isotherm assuming monolayer coverage was applied. However, a Langmuir analysis that assumed only one type of adsorption site failed to reproduce the experimental adsorption isotherm curves; instead a Langmuir analysis on the Langmuir isotherm assuming monolayer coverage on Na+−Y zeolite at 150 °C in vacuum: (A) spectrum measured following 27 h of heating at 150 °C; (B) spectrum measured after a week of heating at 150 °C; (C) spectrum of a sample kept at room temperature for 2 months following the same treatment as that of A.

Among the issues of adsorption and the distribution of guest species in zeolite cavities, adsorption sites within zeolites are of particular importance. Adsorption sites are usually associated with the extra-framework cations and framework oxygens. Of these, the primary adsorption sites for small aromatic molecules are considered to be located at the cation sites. For example, it has been established experimentally (IR [49–52], Raman [53,54], NMR [55–59], neutron diffraction [60,61], small-angle neutron scattering [62,63]) as well as by computer simulation [64,65] that benzene can be localized at two distinct binding sites, cations and windows, within the Na+−Y zeolite supercage. In S1 binding site (four per supercage), benzene is facially coordinated to a supercage 6-ring, 0.27 nm above Na+. In the window site (two per supercage, shared) benzene is centered in the 12-ring window, 0.3 nm from S1. Because of the strong Na+−benzene interaction, binding site S1 is much more stable than the window site. The distribution is considered highly heterogeneous [66] which is reminiscent of the situation within micelles [67]. The big difference is that, while in micelles the equilibrium distribution is attained very quickly because of the high mobility of guest molecules, this is not the case in zeolites due to very slow diffusion [68]. Experimentally, NMR spectroscopy is used to directly probe the guest populations for a high-pressure atomic gas occluded in the zeolite cavities [69,70]. As an example, the distribution of xenon atoms in Na+−A zeolite was described by Poissonian statistics for mean occupancies less than about three Xe atoms per α-cage. At higher loadings, the finite volume of the atom becomes significant, as reflected by an excellent fit of the 129Xe NMR data, with a binomial distribution for the value of the mean occupancy, \( n = \left[ \text{[guest]} / [\text{cage}] \right] \) up to five, with a maximum of seven xenon atoms per α-cage. Then, the hypergeometric distribution comes into play, but even this fails at very high loadings, predicting a larger variance than that actually observed. Thus, even for the simplest case of rare gas atoms, which have the least interaction, both mutually and with the framework, the distribution among the cages is not very simple.

For large aromatic species such as naphthalene [71–73], anthracene [41,74,75], and pyrene [66,76,77], it has been...
shown that the emission spectra in Na\textsuperscript{+}-Y or Na\textsuperscript{+}-X are loading-dependent: the contribution of excimer emission increases at the expense of monomer emission as the loading increases, even at very low mean occupancy (\( n \ll 1 \)). This is considered to be an indication of a heterogeneous distribution within the zeolites, because the excimer emission is considered to arise from more than one molecule occupying the same cage. Detailed analysis has not been carried out to elucidate the distribution law of these molecules, because it is imagined to be no easy task. In essence, one should be aware in zeolites that an average occupancy of unity does not mean that most supercages contain one guest species on the average but rather that most cages are empty, with some being multiply-occupied [78].

2.3 Diffusion

The transport of molecules within the intracrystalline cage network of zeolites is important, both in influencing chemical reactions of the guest species and for the design and application of shape-selective catalysts [79,80]. In usual cases, the molecules introduced externally into zeolites are not fixed at particular sites, but rather migrate by executing a hopping motion from one adsorption site to another within the same cage and occasionally to other cages through one of the connecting windows, unless they are immobilized by a "ship-in-a-bottle" synthesis [81–83]. Typically, intercage hopping assumes a relatively high activation barrier and is a slow process, allowing the guest molecules to stroll around the adsorption sites within a given cage before they jump out [84–86] (Fig. 5).

Reactions controlled by the transport of guest molecules through the zeolite framework are of particular importance in that these can involve triplet states and radicals that may have long lifetimes. On the contrary, at short times (ps to ns), reactions are static and occur between reactants located relatively close to each other.

Depending on the similarities in the sizes of the molecules and cages, the intracrystalline diffusivity can vary over a range of about 12 orders of magnitude, from \( 10^{-16} \) to \( 10^{-28} \text{m}^2/\text{s} \). The values are obviously much smaller than those obtained in solutions, being constrained by the geometries of pores. Of particular interest is benzene, whose diffusivity in Na\textsuperscript{+}-Y and Na\textsuperscript{+}-X was thoroughly investigated both experimentally and theoretically. Among various experimental techniques, the pulsed field-gradient NMR (PFG NMR [87,88]) and quasi-elastic neutron scattering (QENS [89,90]) methods have gained popularity. According to a recent QENS study [90], the values of the self-diffusion coefficients of benzene at 300 K are \( 3.1 \times 10^{-11} \text{m}^2/\text{s} \) in Na\textsuperscript{+}-X (Si/Al = 1.23) and \( 4.6 \times 10^{-11} \text{m}^2/\text{s} \) in Na\textsuperscript{+}-Y (Si/Al = 2.43) for loadings of 1.5–2 molecules per supercage. At room temperature, the diffusivity is almost 2 orders of magnitude lower in Na\textsuperscript{+}-Y than in Na\textsuperscript{+}-X. This reflects the strong influence of cation distribution at this temperature. The activation energy for diffusion in Na\textsuperscript{+}-Y, 33.7 kJ/mol, is about twice that in Na\textsuperscript{+}-X, 17 kJ/mol, at low loading. The diffusivities are known to decrease with increasing loading [90].

The meaning of the self-diffusion coefficient, \( D \), is translated to the mean-square jump distance, \( \langle r^2 \rangle \), according to the Einstein expression in three dimensions [85]:

\[
\langle r^2 \rangle = 6D\tau
\]

(1)

where \( \tau \) represents the time required for a jump. Eq. (1) predicts that, in Na\textsuperscript{+}-Y, in which the cage-to-cage jump distance is 1.1 nm, the average distance traveled by benzene is estimated to be 1.5 cages in 1 ms and 48 cages in 1 ms at room temperature, while in Na\textsuperscript{+}-X, it will be 12 cages in 1 ms and 400 cages in 1 ms. Thus, for species with long lifetimes, intercage migration is definitely an important factor affecting kinetics and mechanism of reactions.

Only a few studies have been carried out so far on the intrazeolite diffusivity of aromatics larger than benzene. For example, the diffusion coefficient of naphthalene in Na\textsuperscript{+}-X and Na\textsuperscript{+}-Y below 350 K was reported to be \( \sim 10^{-16} \text{m}^2/\text{s} \) [94]. We have recently obtained the values of \( D \) for azulene, ferrocene and anthracene, ranging from \( 10^{-15} \) to \( 10^{-16} \text{m}^2/\text{s} \), sufficiently smaller than the value of benzene in Na\textsuperscript{+}-Y, based on the triplet quenching experiment at ambient temperature [68]. It is highly possible that the cage-to-cage diffusivity of the guest species is dependent on the molecular size because of constraints on the diffusive motion imposed by the windows and walls of the zeolite. It has also been

Fig. 5. Pictorial representation of the diffusion of molecules in a zeolite particle. The diffusional motion is classified as two types according to the nature of the activation energy: (1) activation energy for intercage jump and (2) activation energy for intracage jump.
pointed out that the intercage hopping dynamics of benzene are largely affected by the adsorption interaction with the host zeolite: a self-diffusion coefficient as small as \(10^{-18}\) to \(10^{-19}\) m\(^2\)/s was measured for benzene in Ca\(^{2+}\)-Y, in which benzene is strongly held [95].

### 2.4. Sample preparation protocol

Several different methods have been applied for the adsorption of aromatic molecules into zeolites, including sublimation at elevated temperatures under evacuated conditions [96-98], stirring zeolite powders in solutions of aromatic molecules followed by the removal of solvents with evacuation treatments [28], and mixing solid aromatics with zeolite powders in a mortar [99]. Different handling in the procedures for preparing samples as well as the different method of sample preparation sometimes induces contradicting observations even for similar systems. The major cause of the discrepancies observed is associated with the various hydration levels of the zeolites: water could easily be introduced into the zeolites, which have an extremely hygroscopic nature, in the sample preparation procedure.

For example, Thomas and co-workers [100,101] observed in the transient absorption spectra the formation of the radical cations of aromatic molecules and trapped electrons in the form of Na\(^{4+}\) absorbing at 520 nm in Na\(^{−}\)-Y and 550 nm in Na\(^{−}\)-X upon laser excitation of the aromatics. On the contrary, Gessner and Scaino [102] failed to confirm the presence of Na\(^{4+}\) as a counterpart of the radical cations in a similar experiment. Both groups employed the solution method for adsorption. As was pointed out later in the study from our laboratory [72], this contradiction is due to the fact that the absorption spectrum of the trapped electrons are considerably affected by the presence of various amounts of water molecules within the zeolites. Their absorption peak is shifted to longer wavelengths in the presence of large quantities of co-adsorbed water, which might be introduced in the sample preparation procedures.

In other studies, both fluorescence and triplet decay rates of aromatics were reported to be significantly affected by the presence of water in zeolites. Ramanurthy et al. [29] reported that the fluorescence decay rate of pyrene adsorbed into Na\(^{−}\)-Y is smaller with increasing hydration level. Hydration may cause the liberation of the guest molecules from the host zeolite by the action of the water molecule, which has a much stronger interaction with the zeolite and can lie preferentially on the zeolite walls. It has been shown that the enhanced non-radiative decay rates in the adsorbed molecules give rise to the short lifetimes of the S\(_1\) state [103,104]. Another cause of the short lifetimes in the dry zeolites may be the self-quenching of fluorescence by ground-state species, since pyrene and other aromatics with relatively large molecular size tend to form aggregates at the immediate surface of the zeolites, and these aggregates can dissociate in the hydrated zeolites [28,29]. Our study showed that the fluorescence decay rate of anthracene is greater with increasing loading levels in dry Na\(^{−}\)-Y zeolite [41]. Excimer formation is largely responsible for the self-quenching of the fluorescence of anthracene in Na\(^{−}\)-X and Na\(^{−}\)-Y.

The long triplet lifetimes of aromatic species were found to be altered dramatically at various hydration levels in the zeolites [105]. Fig. 6 depicts the decay constants of triplet-state anthracene plotted as a function of the quantity of co-adsorbed water and other solvents.

In dehydrated Na\(^{−}\)-Y (<0.4 wt. % water content), with a triplet decay constant of \(60 \pm 5\) s\(^−1\), the value comparable to that observed in a rigid plastic matrix, poly(methyl methacrylate), was obtained [106,107]. With increasing water content, the decay constant increased once to a value that is about 3 orders of magnitude larger than that in the dehydrated zeolite and then again decreased to a value more or less similar to the original one in the presence of water in quantities sufficient to fill the total pore volume. This peculiar behavior of the decay constant of triplet state anthracene was dependent both on the loading level of anthracene and on the intensity of laser light employed for excitation. The observation was rationalized by the different mobilities of anthracene within the supercage networks of the zeolite being strongly dependent on the water content, leading to the self-quenching and triplet-triplet annihilation. The intercavity motion of anthracene as well as the intracavity motion as a function of water content initially increases because of the cancellation of adsorption interactions of the guest anthracene with the zeolite walls, followed by a significant decrease due to blocking of access to the neighboring cages and the reduction in the free volume inside the cages by water molecules. As is evident in Fig. 6, solvents

![Fig. 6. Decay constants of triplet-state anthracene plotted as a function of the quantities (cm\(^3\)/g) of various solvents for samples with anthracene loading level of 1.0×10\(^−4\) mol/g in Na\(^{−}\)-Y (pore volume: 0.78 cm\(^3\)/g) at similar laser intensities. Symbols: (O) H\(_2\)O; (●) D\(_2\)O; (▲) acetonitrile; (□) isopropyl alcohol; (△) methanol; (●) n-hexane; (▲) pyridine.](image-url)
that a strong affinity towards zeolite frameworks (alcohols, acetonitrile, pyridine, etc.) have a similar but less pronounced effect on the triplet lifetime of anthracene, but those with weak interactions with the zeolite (n-hexane, benzene) have practically no effect.

Solvent molecules employed for the adsorption of aromatic species, usually alkanes such as n-hexane, which remained in samples after preparation due to insufficient evacuation treatment, affected the photophysical behavior of guest species in a different way [74]. Although they do not appear to interfere appreciably with the adsorbed state of guest aromatics on the interior surface of the zeolite, they do form complexes with the guest aromatics. Such an example is shown in Fig. 7 for the fluorescence spectra of anthracene adsorbed in Na\(^+\)Y in the presence of n-hexane.

In this case, a gradual red shift in the fluorescence spectra with increasing amount of n-hexane is indicative of complexes between anthracene and n-hexane at various molecular ratios. In spite of this fact, it was found that solvents such as n-hexane do not affect dramatically the fluorescence lifetimes or triplet decaytimes of guest aromatic species, which makes it difficult to perceive them even when present in samples.

These examples call for the necessity of taking extreme care in removing both water as a contaminant from solvents and/or moisture, and solvent molecules themselves employed for adsorption when aromatic species are adsorbed conventionally using solvents. For removing water as well as n-hexane or dichloromethane, evacuation for more than 12 h at less than 0.1 Pa at an elevated temperature of about 100 °C is recommended unless thermal reactions or evaporation of the guest species is a problem; this treatment gave a water content of less than 0.4 wt.% for Na\(^+\)Y. Note that evacuation at room temperature even for a prolonged period is not very effective for removing water and n-hexane. Considering the lower reliability of the dehydration level in the adsorption method from solution, the adsorption through a gas phase diffusional process in vacuum appears advantageous. However, this adsorption method tends to end up with a heterogeneous distribution of guest molecules, and heating at an appropriate temperature for a prolonged period (usually 2–3 weeks and sometimes even more than 1 month) is necessary to allow guest species to diffuse through the entire cage network. To avoid the problems of solvent remaining in the samples and of possible damage due to heating, fluorocarbons such as perfluorohexane can be used as a solvent if the molecules of interest are sufficiently soluble [108].

It should also be noted that the glass sealing of the samples is absolutely necessary to protect them from contamination by moisture. Most strikingly, unsubstituted aromatics such as phenanthrene, anthracene, biphenyl, naphthalene, pyrene, etc., adsorbed into Na\(^+\)X and Na\(^+\)Y zeolites form crystals in the presence of water and other solvents bearing strong affinity for the zeolites in large quantities, which can nearly fill the total pore volume [74,109]. Similar phenomena were observed in zeolite L, too [110]. This is a serious problem because zeolite samples adsorbed with these aromatic species eventually produce crystals by absorbing moisture from air and no longer keep the guest species in the original adsorbed state when left without being sealed.

Thus, we should point out that some photochemical studies in zeolite systems might have problems due partly to inappropriate dehydration procedures and partly to insufficient isolation method from air, e.g. use of septum seals after nitrogen purging of samples. These operations may cause a peculiar observation of aging of guest species in a period of weeks and months due in part to slow evaporation of solvents used for adsorption and in part to penetration of water into the cages from the air [111]. The exact mechanism of the aging is not clear, but continuous diffusion and eventual crystallization of the guest molecules caused by co-adsorbed water seems to be responsible for the observed changes in the fluorescence spectra of pyrene in zeolites. Thus, the remark can be made that a critical view should always be taken in reading the literature related to zeolite photochemistry as to the methods and handling in sample preparation procedures, since no standard procedures generally applicable to many guest molecules are available at this moment.

2.5. Diffuse reflectance spectroscopy

Since first implemented in 1981 by Wilkinson and Kessler [112], the diffuse reflectance laser photolysis technique

![Fig. 7. Absorption and emission spectra (uncorrected, λ\textsubscript{ex} = 355 nm) of anthracene adsorbed into dehydrated (water content: <0.4 wt.%) zeolites and in solution: (A) 5.0 × 10\(^{-4}\) mol/g in Na\(^+\)Y; (B) 5.0 × 10\(^{-5}\) mol/g in the presence of 0.12 cm\(^3\)/g n-hexane in Na\(^+\)Y; (C) 5.0 × 10\(^{-6}\) mol/g in the presence of 0.24 cm\(^3\)/g n-hexane in Na\(^+\)Y; (D) 1.0 × 10\(^{-7}\) mol/dm\(^3\) in n-hexane solution. The absorption spectra in (A)–(C) are represented by Kubelka-Munk units, while the spectrum in (D) is represented by absorbance.](image-url)
has gained popularity for surveying the transient species in various non-transparent solids such as organic microcrystals, powdered solid polymers and inorganic semiconductor powders [113–117]. The technique has been successfully applied to photophysical and photochemical investigations of molecules adsorbed on solid supports, including silica gel, alumina and zeolites [3]. The optical arrangement for experiments and the methods of data analysis have been established by Wilkinson’s group [113–115]. The time resolution of detection systems was initially limited to the microsecond region but was later extended to the picosecond and femtosecond domains by utilizing a pump–probe method in which an ultra-short white-light continuum generated by focusing a fundamental laser beam was employed as a monitor light source. The laser beam was irradiated at right angles to a powder sample contained in a 2 mm optical path-length Suprasil cell. The monitor light beam was collected with a lens (Ø 40 mm, f = 100 cm) and introduced into a polychromator. The light signal (400–900 nm) was detected either with a photomultiplier or a gated photodiode array detector with an image intensifier. The time resolution was limited to the microsecond range for the detection with a photomultiplier, because the diffusely reflected light was so weak in intensity that the photomultiplier need to be wired for full-stage (nine dynodes for R928 (Hamamatsu)) for amplification, and a signal cable need to be hooked up with a load resistor larger than 500 Ω, this sacrifices the time resolution significantly. It is also the case in the photomultiplier detection system for the solid samples that the early stages of the event are disturbed by the scattered light from the laser pulse and/or intense fluorescence emission. On the other hand, the detection with a gated diode array using a pump–probe method allowed the time resolution to reach 5 ns by eliminating spontaneous emission and scattered light from the laser. In this system, the detection wavelength was extended to the near-IR region (900–1600 nm) by using a red-sensitive InGaAs detector [71].

With the diffusely reflected light from powdered samples being used as the monitoring light, the transient absorption spectra in the diffuse reflectance laser photolysis should be obtained with a treatment different from that for spectra in ordinary transmittance mode measurements. The Lambert–Beer law is not applicable to represent the transient absorption, because the diffusely reflected light consists of a group of light beams with various optical pathlengths from the sample. Instead, the Kubelka–Munk function has been applied to describe the steady-state absorption in the reflectance mode [121]:

\[ F(R) = \frac{(1 - R)^2}{2R} = \frac{k}{3} \]

where \( F(R) \) represents the Kubelka–Munk remittance function; \( R \), the diffuse reflectance from a sample; \( k \), the absorption coefficient; and \( s \), the scattering coefficient. Thus, the plots of \( F(R) \) versus wavelength represent the absorption spectra if the scattering coefficient is wavelength independent. The Kubelka–Munk function has been extended to time-resolved spectroscopy, and the transient absorption intensities were expressed in terms of absorption (\%)

\[ \text{absorption (\%) = } 100 \times \left( 1 - \frac{R}{R_0} \right) \]

in which \( R_0 \) denotes the intensity of the diffusely-reflected light of the probe pulse with excitation, and \( R \), that without excitation.

It is important to note that the value of absorption (\%) is not always a linear function of the concentration of the transient species produced in the sample, and a linear relationship holds only at small values of absorption (\%) [115,120]. The saturation phenomena of absorption (\%) are dependent on the value of \( k/s \). For the samples with small values of \( k/s \), the deviation from linearity is appreciable even at a few percent of the absorption (\%) value, whereas for large values of \( k/s \), linearity holds at more than 15%.
The value of $s$ is larger for particles with smaller size and increases linearly with the average surface area of particles per unit volume of the sample, since the scattering of light takes place at interfaces between particles and air and the number of scattering events per unit volume in the powder is proportional to the surface area. In adsorbed systems, the scattering of light mostly results from host supports such as zeolites, and $s$ is approximated by the value for the host material. Thus, the guest species is required to have a large value of $k$ or $c$ ($k = 2.303cc$, where $c$ is the molar absorption coefficient and $ε$ is the molar concentration) to allow a good linear relationship between absorption (%) versus the intensity of laser light for excitation first be checked for a singlet or triplet excited-state species, which can be generated as a linear function of laser intensity. Then, one should check the laser intensity-dependent behavior of a given species before kinetic analyses for the species are performed.

A precaution is necessary to prevent sample damage due to repeated irradiation of laser light: a colored spot may sometimes develop after several shots. No permanent remedy is available for solid samples, although a flow method can be used for solutions. Either shaking samples after every few shots or changing the position of irradiation on samples routinely can minimize the change in reflectance caused by the colored sample solids. It is also important that the excitation intensity be as low as possible for the least possible damage of samples. Notably, monitor light occasionally causes an artifact in the decay of transient species; two examples are given here for such cases. In the first case, the transient absorption signal of a trapped electron, Na$_4$ anthracene, was found to decrease by a continuous Xe-arc lamp through IR-cut-off filters and a 10 cm-long water filter [122]. The filters are supposed to prevent the heating of the sample. It was found that the decay rate is dependent on the intensity of the monitor light; the decay rate is low when the monitor-light intensity was decreased using neutral density filters. In contrast, the decay rate was very slow when monitored with a pulsed Xe lamp with a duration of 10 μs. The phenomenon observed is ascribed to the photobleaching of trapped electrons. Similar phenomena are well-investigated for trapped electrons produced by γ-irradiation in low-temperature matrices [123-125]. In the second case, the decay rate of the triplet-triplet absorption signal of anthracene in the Na$_4$ zeolite was found to depend on the intensity of monitor light, and again the decay rate was lower as the light intensity was decreased (Fig. 9) [68].

In this case, the temperature rise in the sample caused by the small amount of heat generated by irradiation must be responsible. The two examples tell us the importance of taking extra care about the intensity of the monitoring light when working with a transient species with a long lifetime in solid samples. Preferably, the use of monochromatic monitoring light is recommended.

Transient absorption spectroscopy in terms of diffusely reflected light was found to carry a certain limitation in the temporal resolution of transient absorption signals in the femtosecond time domain [120]. This is because ultra-short (much less than the picosecond scale) light pulses of both excitation and probe light are temporally broadened due to numerous times of refraction, reflection and diffraction in light-scattering materials before arriving at the sample surfaces [126]. Thus, the time profiles of transient absorption depends on the optical properties of the samples, namely $k$ and $s$. In the case of small $k$ for a given value of $s$, the concentration of excited species near the sample surface gradually increases with time, and its depth profile changes up to several tens of picoseconds. This phenomenon leads to a decay time much longer than the lifetimes of a given transient species, given that the lifetimes are less than a few picoseconds. On the other hand, for a sample with a large $k$ value, excited species are populated only at or near the surface due to the limited penetration depth of the excitation light, and the temporal change in the depth profile is completed within a few picoseconds. These features enable the decay of absorption (%) to correspond faithfully to the concentration of the transient species. In effect, the temporal resolution is less than a few picoseconds, equivalent to that of transmittance mode experiments under an appropriate optical condition, such as a large extinction coefficient at the excitation wavelength with a small scattering coefficient. It should be borne in mind, however, that the time resolution might be extended to...
several tens of picoseconds under inappropriate optical conditions.

3. Molecular photophysics and photochemistry in zeolites

3.1. Confinement effect

Spatial confinement in the cavities of zeolites is expected to provide molecules with geometric restrictions due to the framework, which may lead to unusual photophysics and photochemistry of the guest species. This idea was tried with a molecule whose size is similar to the dimension of the entry aperture, and thus the host/guest complex was expected to fit in very tightly. Alternatively, in order to induce a pronounced confinement effect, a bulky molecule that cannot enter through a pore opening was incorporated with the ship-in-a-bottle synthesis [81–83]. Further extension of the idea of confinement has led to the concept of electronic confinement in which it was anticipated that the molecular orbitals of the guest species undergo severe deformation due to the geometrical constraints imposed by the zeolite walls.

A number of research efforts have been carried out on steric confinement. Another important aspect of the confinement is that zeolite cavities may prevent or restrict the approach of guest molecules, in particular, reactive intermediates. Here, we review from the two aspects, static and dynamic, confinement within zeolites.

Cationic dyes are a good example of how monomer–dimer (or aggregate) equilibria are dramatically affected by the confinement in zeolites [127,128]. Thionine (TH⁺), which is smaller in size than the channel diameter, was found to be incorporated in the monomer form in the main channels of zeolite K⁺-L via ion exchange; however, methylene blue (MB⁺) which is larger than the channel diameter, could not enter the channels but instead remained on the exterior surfaces, forming dimers and aggregates.

The spatial restriction by the channel walls prevents the formation of parallel dimers (H-type aggregates) inside the channel. Most interestingly, Carzaferri’s group showed that TH⁺ molecules first adsorb on the outer surfaces in the dimeric form and slowly enter the channels in a monomeric form [127]. This clearly shows that the spatial regulation by the channel walls depends on the guest species to be incorporated. Since the cationic dyes have a tendency to form aggregates in solution and these aggregates cause photodegradation of dye molecules, incorporation into zeolites is one of the promising ways to improve the photostability of dyes.

Association of the methylviologen radical cation (MV⁺⁺) was investigated in zeolites by Yoon and co-workers [129]. The dimerization of MV⁺⁺ was observed, from the measurement of absorption spectra, exclusively in zeolite L and not in the large-pore zeolite Y or in narrow-channel ZSM-5 when incorporated into dehydrated zeolites.

This finding, which is in striking contrast with the observation of TH⁺ in zeolite L, is due to the smaller short-axis length for MV⁺⁺ than for TH⁺. As observed for MV⁺⁺, neutral molecules such as biphenyl, naphthalene and anthracene were also found to form a ground-state dimer (possibly with sandwich-type configuration), which gives rise to excimer emission on photoexcitation within the straight channels of zeolite L [75]. This fact suggests that molecules with a small lateral width are forced to lie along the channel wall within zeolite L owing to a monodirectional geometric restriction. Molecules that have a short-axis of size similar to that of MV⁺⁺ can fit into the channel, forming a sandwich structure. This geometry is expected to bring about a rather tight fit, and indeed, a remarkably strong interannular interaction was observed between two anthracene moieties, as evidenced by the electronic absorption spectrum. Overall, the channel-type zeolite L exhibits larger structural regulation for adsorbed species over zeolite Y with large spherical pores.

The tight fit of molecules into the zeolite pores and channels enables the observation of room temperature phosphorescence (RTP). Although Ramamurthy et al. reported previously [99,130], the remarkable enhancement of phosphorescence from aromatic species adsorbed in heavy atom-exchanged zeolites, as will be described in more detail in Section 3.2, RTP was observed in zeolites without the assistance of heavy-atom perturbations. A study from our laboratory showed that 9-ethylcarbazole (ECZ) and
other aromatic species, e.g. naphthalene, phenanthrene, 1,2,4,5-tetracyanobenzene, etc. give rise to phosphorescence emission with an appreciable intensity in K*-L zeolite at room temperature despite the fact that RTP is extremely weak in zeolite Y, which has large spherical pores [75].

The phosphorescence lifetime of ECZ in K*-L was measured to be 2.6 s at 296 K, compared to 7.6 s at 77 K, and this long lifetime suggests that the rate of radiationless deactivation from T1 is significantly reduced. Thus, it was concluded that the tight fit into the channels and resultant increased structural rigidity are largely responsible for RTP. Earlier than our work, Scaiano and co-workers reported the observation of RTP from acetophenone and β-phenylpropophenone incorporated into silicalite [131], an all-silica zeolite with narrow channels. Since aromatic ketones have an intersystem crossing quantum yield of almost unity, the observation of RTP appears much easier. Nevertheless, the steric restrictions imposed on the ketones in the channels of silicalite are very important for the observation that pioneered RTP in zeolites. A similar observation of RTP was reported for naphthalene in ZSM-48 (pure silica zeolite having unidimensional channels with dimensions of 0.57 nm × 0.51 nm) and 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) in silicalite and Theta-1 (high-silica zeolite with Si/Al = 30 and monodirectional channel-type zeolite with an oval channel of 0.46 nm × 0.57 nm) [132].

Marquez et al. proposed an idea that the influence of the cavity dimensions on the electronic structure of some guest organic molecules incorporated within zeolites can be related to the quantum confinement concept [132–134]. This picture was correlated with an “electronic confinement effect” in which the electron density of the guest is constrained to be mainly localized within the zeolite cavity as a result of strong short-range repulsion with the electrons of the zeolite walls [135]. This idea was first applied for the interpretation of the absorption and fluorescence spectroscopic properties of anthracene incorporated in zeolites with various pore sizes (Na+-Y, Na+ -mordenite, Na+-ZSM-5 in the order of decreasing pore size) [133]. A larger bathochromic shift of the 0-0 transition of the electronic absorption spectrum in zeolites with smaller pore sizes was directly ascribed to the electronic confinement effect. The concept of electronic confinement is based on a molecular orbital (MO) treatment. Later, these workers obtained the same conclusion from the absorption and emission spectroscopic observation of naphthalene [132] and DBH [134] by applying the same analysis. Notably, they incorporated these molecules in pure silica zeolites, which contain few cations, in order to study exclusively the influence of the confinement effect, avoiding the interference of electrostatic effects due to framework and extra-framework cations.

A few questions can be raised regarding this work. The idea of electronic confinement is fascinating if solid experimental proof is obtained by using well-suited guest molecule/zeolite pairs with carefully executed procedures. First of all, with normal adsorption techniques [96–99], it is extremely difficult to incorporate molecules externally into zeolites with such narrow spaces that they may provide a large enough constraint on the guest species to bring about deformation of its MOs. They will be simply expelled from the pores and channels and may stick on the outer surfaces. In this sense, anthracene may not be very appropriate for such a purpose. Anthracene molecules are safely assumed to go into the cavities of zeolites X and Y but scarcely go into the small channels of Na+-ZSM-5. Besides, research from our laboratory showed that anthracene forms a ground-state dimer, which gives an appreciably distorted absorption spectrum even at very low loadings due to excitonic interannular interaction forced by the channel walls and affords a broad, red-shifted excimer emission spectrum in the narrow channels of zeolites K+-L and Na+-L [75]. Remember that the size of the entry aperture of the channel for zeolite L is similar to that of mordenite. Thus, we can observe a more red-shifted 0-0 band of the absorption spectrum in zeolite L than in Na+-Y; but for anthracene this is not due to the electronic confinement effect. The tendency of forming aggregates on the surfaces of zeolites with small cavities also makes it difficult to detect the minute differences in the spectra dependent on the zeolite type. A further concern is the formation of anthracene crystals, which give red-shifted absorption and emission spectra [74,110]. They can easily be formed when samples adsorbed with anthracene are left in the open air due to hydration. A similar discussion may apply to naphthalene and DBH because of the very poor spectra, which make it difficult to be convinced by the arguments given in the literature. Extra effort in experimental work is needed to verify the idea of electronic confinement by zeolites.

Investigations aimed at pursuing large confinement effects were carried out with bulky molecules incorporated using the ship-in-a-bottle synthesis. García and co-workers [136] studied the photophysical properties of 2,4,6-triphenylpyrylium (TPP+ ) and substituted tritylium ions encapsulated within Y, β, and MCM-41 zeolites.
The effect of a tight fit was observed as simultaneous emission of fluorescence ($\lambda_{\text{max}} = 470$ nm) and RTP ($\lambda_{\text{max}} = 560$ nm) of TPP$^+$ within H$^+$-Y and La$^+$-Y, whereas only fluorescence was detected for TPP$^+$ in extra-large-pore MCM-41 or on silica. The characteristic T$_1$–T$_n$ absorption spectrum of the TPP$^+$ was detected with transient absorption measurements. For TPP$^+$/La$^+$-Y, the maximum of the broad 450–600 nm absorption was somewhat shifted to longer wavelengths (peaking at 550 nm) with respect to TPP$^+$/MCM-41. They also noted an increase in the extinction coefficient for the band in zeolite Y compared with that in MCM-41 or the spectrum in solution. Although they ascribed these changes to molecular orbital distortions resulting from the confinement of the molecule within the restricted space of the cavity, the effect of confinement is not very dramatic, judging from their result.

The 9-(4-methoxyphenyl)xanthylium ion (AnX$^+$), a bulky cation, has also been prepared by a ship-in-a-bottle synthesis within the supercages of zeolites Y [137]. No fluorescence has been observed for AnX$^+$ at room temperature in solution, and this anomaly was rationalized assuming a deactivation by intramolecular quenching of the xanthylium moiety by the anisyl substituent occurring in a twisted conformation. RTP was observed from AnX$^+$ in the zeolites. Besides, the triplet-state of AnX$^+$ was observed in the zeolites as a long-lived species (tens of microseconds) with transient absorption spectroscopy, while it has not been observed in solution. These results indicate that the intramolecular quenching of the xanthylium moiety by the anisyl substituent is less effective in the restricted environment provided by the zeolite cage.

The confinement effect was stimulated with the aid of co-adsorbed solvent molecules within zeolites. Scaiano et al. [138] found that the incorporation of large concentrations of pyridine leads to an increased lifetime of triplet p-methoxy-β-phenylpropophenone adsorbed in Na$^+$-Y. In the case of p-methoxy-β-phenylpropophenone, the triplet lifetime is normally determined by intramolecular quenching by the β-phenyl ring. The observed enhancement of the triplet lifetime was regarded as an indication of reduced ability to undergo conformational change as the pyridine occupancy of the supercages increased. Thus, the extent of the compact environment found by guest molecules upon addition of large amounts of co-adsorbed molecules and an increased local viscosity within the supercages of the zeolite provided by the co-adsorbed solvents was suggested to slow the intramolecular quenching process. It should be noted that the effect of co-adsorbed solvent molecules is critically dependent on the nature and quantity of solvents introduced and a certain precaution is necessary, because the solvents usually increase the mobility of guest species within the zeolites [105,139].

As an example of the dynamic confinement effect (restriction of movement), Turro’s group investigated the combination reaction of benzyl radicals and diphenylmethyl radicals, produced by the photolysis of DBKs and 1,1,3,3-tetraphenylacetone on MFI zeolites [47,48,140]. The parent molecules are too large to enter the channels and are forced to reside on the external surfaces. Two types of adsorption sites, a capping position on the channels or hole (site I) and the framework surface (site II) are assumed based on the Langmuir isotherm study of adsorption. The ESR and fluorescence spectroscopic studies as well as product analyses revealed that the radicals with a smaller size than the channel diameter can diffuse into the channels, while those too bulky to fit in the channel diffuse on the outer surface, leading to combination forming stable products. Here, the benzyl radicals result in the combination reaction both on the external surfaces and within the channels; on the contrary, a portion of the diphenylmethyl radicals are trapped within the channels and are found to persist for many weeks.

Another piece of research in Turro’s group also discovered that a diphenylmethyl radical (DPM$^*$) generated by photolysis in a MFI zeolite, the sodium form of LZ-105, is extremely persistent and reacts reversibly with oxygen to form a peroxy radical (DPMO$_2$)* at room temperature [141].
The DPM• was detected both by an ESR spectrum and by a fluorescence spectrum. DPM• is rendered persistent through a “supramolecular steric effect” (translated as dynamic confinement effect), which severely inhibits the approach of two guest species, leading to radical–radical reactions.

3.2. Interaction with cationic sites

In their pioneering work, Ramamurthy et al. [99,130] reported that external heavy-atom effects of associated cations on the guest allocated within zeolite supercages increase remarkably the efficiency of intersystem crossing, leading to triplet states. In some cases, this external enhancement can be comparable to effects caused by covalently bonded heavy atoms. For example, the phosphorescence of aromatic species such as naphthalene incorporated into Rb⁺-X and Cs⁺-X at 77 K was observed, while only the fluorescence was detected in Na⁺-X and Li⁺-X. A much greater effect of the charge-compensating cations was observed in Ti⁺-X, in which even RTP was observed for the incorporated aromatics. Similar systems were investigated with transient absorption spectroscopy in our laboratory [142], and a more elaborate picture of the interaction between Ti⁺ ions and guest aromatic species was obtained.

Transient absorption measurements were carried out for anthracene, phenanthrene and naphthalene incorporated into Na⁺-X, Cs⁺-X (68% Cs⁺) and Tl⁺-X (97% Tl⁺), and the recorded spectra are depicted in Fig. 10. The spectra in both Na⁺-X and Cs⁺-X are quite similar to those of triplet–triplet (T₁–Tₙ) absorption in solutions. Note, however, that the absorption intensities in Cs⁺-X are much greater for the samples with a similar loading level at a constant excitation energy than those in Na⁺-X due to heavy atom effect. Strikingly, the transient absorption spectra in Ti⁺-X are different from those in Na⁺-X and Cs⁺-X: remarkably broad and featureless spectra with a red shift are obvious. Nevertheless, the transient spectra in Ti⁺-X are assigned to the T₁–Tₙ absorption of these aromatics on the basis of a similarity of the decay profiles of transient absorption and phosphorescence. Phosphorescence intensities are considerably higher in Ti⁺-X, although the phosphorescence spectra in Ti⁺-X are not much altered from those in Cs⁺-X; slightly broader envelopes and small red shifts in Ti⁺-X were noted. These observations are rationalized on the grounds that triplet complexes of the aromatic species with the charge-compensating cations are formed in the Ti⁺-X system.

The triplet complexes were observed in zeolites, but not in solutions. In solution studies [143–145], it was demonstrated that the fluorescence quenching of a number of aromatic hydrocarbons by metal ions including Ti⁺ and Ag⁺, leads to the enhanced formation of the triplet-state of the aromatic species. Among the quenchers, the quenching rate constants of Ti⁺ and Ag⁺ were exceptionally larger than those of the pure heavy-atom quenchers, Cs⁺ and Xe. The quenching mechanism due to non-fluorescent complex formation, followed by a rapid intersystem crossing, was suggested, but no experimental proof has been obtained. Thus, the triplet complexes detected with the transient absorption spectra are considered as a precursor that was sought in previous solution studies [143–145]. The observation of the triplet complexes in Ti⁺-X is one of the intriguing examples that demonstrate the usefulness of the zeolite that geometrically fixes labile species in solution.

Scainano and co-workers [146] demonstrated the different effects of charge-compensating cations on the excited-state behavior of guest species; the interaction of Brønsted and Lewis acid charge-compensating cations of zeolite with 1,1-diphenyl-2-propane (DPA) and 1,1,3,3-tetraphenyl-2-propane (TPA) can divert their normal photochemical behavior, which is characterized by the formation of diphenylmethyl radicals (DPM). Laser photolysis of DPA included in Na⁺-Y and Na⁺-X zeolites generated a transient...

![Fig. 10. Transient absorption spectra of aromatics incorporated into Na⁺-X (top), Cs⁺-X (68% of Cs⁺) (middle), and Ti⁺-X (97% Ti⁺) zeolites at a delay of 1 μs upon excitation with a laser pulse: (A) anthracene excited at 351 nm; (B) phenanthrene excited at 351 nm and (C) naphthalene excited at 248 nm.](image-url)

absorption that is reasonably close to that reported for diphenylmethyl radical (DPM•) in solution:

\[ \text{Ph}_2\text{CHCOCH}_3 \xrightarrow{hv} \text{Ph}_2\text{CH}^+ + \text{COCH}_3 \]

Contrastingly, the laser photolysis of DPA in a de-aluminated and H\(^+\)-exchanged Y zeolite (HDY) led to a transient absorption consisting mainly of DPM carbocation (DPM\(^+\)) with a minor contribution of DPM•. HDY has been indicated to possess a nearly uniform distribution of the strength of the Brønsted acid sites, and the ground-state absorption characteristics of incorporated DPA suggested the absence of an \( n \rightarrow \pi^* \) band due to the C=O chromophore owing to protonation at the acid sites. Thus, a mechanism in which DMP\(^+\) was generated directly from the excited states of the conjugate acid of the DPA was suggested.

Enhanced formation of DPM\(^+\) relative to the yield of DPM• was noted for the photoexcitation of DPA adsorbed in Zn\(^{2+}\)-Y that contains only Lewis acid sites. This finding suggests that the modification of the excited-state reaction takes place regardless of the Lewis or Brønsted acid nature of the zeolite sites.

Close inspection of fluorescence spectra dependent on the degree of hydration as well as on the presence or absence of cations revealed the notable interaction of cationic sites with aromatic species such as anthracene in Na\(^+\)-Y zeolite [74]. This is reminiscent of the “cation–π interaction”, which has attracted much attention from a theoretical point of view. Several examples of the cation–π interaction have been given [147–149], including the clustering of alkali metal ions with aromatics and olefins in the gas phase, the complexation of cations with calixarenes in solution, and the binding of proteins with cationic ligands or substrates in biological systems. This concept also applies to the nature of the adsorption of aromatics into zeolites, as has been shown for benzene [49–65]. Fig. 11 compares absorption and emission spectra of anthracene adsorbed into low loading Na\(^+\)-X, Na\(^+\)-Y, USY and n-hexane solution.

On increasing the quantity of water, the emission spectral bands sharpen and finally resemble those in USY. Therefore, the broadening of the anthracene emission spectra coincides with the strength of the cation–π interaction. For pyrene, the broadening of the emission spectrum in the zeolite Na\(^+\)-X...
and Na\(^+\)-Y is appreciable, and this was also indicative of the cation–π interaction [150].

A more general consequence of the presence of charge-compensating cations can be related to the electrostatic field within the zeolite. Light charge-compensation cations such as lithium ions have been suggested to exert a large effect due to their small size, giving rise to high charge density [5,7]. This effect of lithium ions has been described as the “light atom effect” by Ramamurthy and co-workers who utilized this effect for the control of photophysical transformations within zeolites [5,7]. Also, the general trend of the electrostatic field generated by the charge-compensating cations within the zeolite has been explored with fluorescence probes that normally sense solvent charge-compensating cations such as lithium ions have been suggested to exert a large effect due to their small size, giving rise to high charge density [5,7].

Thus, the electrostatic field around the charge-compensating cation: the yield is much higher in Li\(^+\)- and Na\(^+\)-Y than in Rb\(^+\)- and Cs\(^+\)-Y. As shown in scheme, the reaction was assumed to involve an intermediate, a peropy radical:

They considered that Li\(^+\) and Na\(^+\) provide more stabilization to the O\(^2−\) than the larger cations such as Rb\(^+\) and Cs\(^+\). Thus, the electrostatic field around the charge-compensating cations may play a decisive role in the feasibility of ET from the radical to O\(_2^−\).

3.3. Interaction with the zeolite framework

Interaction of guest species with the zeolite framework is mainly associated with the electron-donating nature of the zeolite. As such, there exists an increasing understanding that the zeolite framework is more active than expected before. Here, we give a few examples.

Thomas and co-workers [152,153] explored the reaction of photo-excited pyrene incorporated into a basic zeolite, a partially cesium-exchanged X and Y zeolite (Cs\(^+\)-X and Cs\(^+\)-Y). At the low loading level of 5 × 10\(^−6\) mol/g, the laser photolysis experiment afforded a transient absorption spectrum consisting of the band of the radical cation of pyrene (Pyr\(^+\)) and that of the radical anion of pyrene (Pyr\(^−\)).

These workers assumed that the ET from the basic site of the zeolite to the excited singlet state (1Pyr\(^\ast\)) of pyrene is responsible for the formation of Pyr\(^+\)*. In their system, the simultaneous formation of Pyr\(^+\)* and Pyr\(^−\)* suggested a possible ET from pyrene in an acidic environment to pyrene in a basic environment on photo-excitation as an alternative mechanism. However, they excluded this possibility on the grounds that ET requires both donor and acceptor to be in close proximity, whereas the sufficiently low loading level of the pyrene employed implies that a great majority of the pyrene molecules are located in different cages. Thus, their point is that Pyr\(^+\)* was produced through the ET from the basic site in the zeolite to 1Pyr\(^\ast\) independently from Pyr\(^−\)*, which is formed by the ET from 1Pyr\(^\ast\) to the acid site within the zeolite.

Factors affecting Pyr\(^+\)* formation were investigated. A high yield of Pyr\(^+\)* was obtained in zeolite X with respect to that in zeolite Y. The yields of Pyr\(^+\)* in both zeolites follow the same sequence of Cs\(^+\) > Rb\(^+\) > K\(^+\) > Li\(^+\) for the charge-balancing cation-exchanged zeolites. These results suggest that the basic nature of the zeolite is responsible for the reaction. In addition, the formation of Pyr\(^+\)* was suggested to follow a single-photon process on the basis of the linear changes of the yield of Pyr\(^+\)* as a function of excitation light intensity in K\(^+\)- and Cs\(^+\)-exchanged X and Y zeolites. This observation is considered to be the foundation for the assumption of a photoinduced ET from the zeolites.
acceptors such as 1,2,4,5-tetacyanobenzene (TCNB) and other cyanoaromatics were incorporated within the zeolites, and their redox properties in the excited-state were pursued with the laser photolysis experiment.

Three types of faujasite zeolites with increasing order of electron-donating ability, i.e. USY < Na\(^+\)-Y < Cs\(^+\)-Y (60 at.% of Cs\(^+\)), were employed as host materials. Fig. 13 compares the transient absorption spectra upon excitation of TCNB at 266 nm in the three zeolites under similar experimental conditions.

In USY, the transient absorption bands peaking at 380 and 615 nm were assigned to those of triplet-state TCNB, whereas in Na\(^+\)-Y and Cs\(^+\)-Y, an additional new band ascribable to the radical anion of TCNB, TCNB\(^{-}\), was observed with a peak at 474 nm. Note that a linear relationship was obtained between the yield of TCNB\(^{-}\) and the laser power applied both in Na\(^+\)-Y and in Cs\(^+\)-Y; thus, the formation of TCNB\(^{-}\) was inferred to follow a single-photon process. This finding suggested the occurrence of ET in the excited-state of TCNB in the zeolites with sufficiently basic nature.

Fluorescence decay curves measured for TCNB in the three zeolite systems are depicted in Fig. 14. Apparently, a faster decay was observed in zeolites with stronger basic sites, which indicates the occurrence of fluorescence quenching for TCNB adsorbed in zeolites with electron-donating nature. Thus, it was concluded that the ET from the electron-donating sites within the zeolites, Na\(^+\)-Y and Cs\(^+\)-Y to the excited singlet state of TCNB (\(^1\)TCNB\(^\ast\)) was unambiguously observed:

\[
\begin{align*}
1\text{TCNB}^\ast + \text{zeolite} &\rightarrow \text{TCNB}^- + \text{zeolite}^+ \\
3\text{TCNB}^\ast + \text{zeolite} &\rightarrow \text{TCNB}^- + \text{zeolite}^+ 
\end{align*}
\]

Additionally, in Cs\(^+\)-Y, the time evolution of the transient absorption signal of TCNB\(^{**}\) showed an indication of the ET from the zeolite to \(^3\)TCNB\(^\ast\):

\[
\begin{align*}
\text{TCNB}^\ast + \text{zeolite} &\rightarrow \text{TCNB}^{**} + \text{zeolite}^* 
\end{align*}
\]

Thus, the absorption signal of TCNB\(^{**}\) evolved in two stages, a fast rise within the duration of the laser pulse and a slow rise in the microsecond time scale, which coincides with the decay of the triplet signal. Remember that the oxidation of zeolites is considered to take place at specific sites such as the framework oxygens at the 12-membered ring.

The absorption bands of CT complexes formed within zeolites were also affected by the electron-donating nature of the zeolites [157,158]. A larger hypsochromic shift was observed for the peak position of the CT absorption band in the zeolite with increasing electron-donating ability. Additionally, ground-state species such as MV\(^{2+}\) [158] and
I$_2$ [159] incorporated in zeolites exhibited a similar phenomenon, depending on the basic nature of the zeolites, with the trend, however, in reverse. On going to greater basicity of the zeolite, a larger bathochromic shift was observed for MV$^{2+}$ while a hypsochromic shift was observed for I$_2$.

The example given thus far in this section is associated with a CT interaction in the excited-state of the guest species, leading to ET from the zeolite framework to the guest species. Cozens and co-workers showed another type of participation of the zeolite host in reaction: the zeolites react by nucleophilic attack with a carbocation, 4-methoxycumyl cation, depending on their basicity [160]. They investigated the reactivity of this carbocation, using nanosecond laser photolysis in non-acidic zeolites.

The carbocation has a relatively short lifetime, in the ms range, in dry alkali metal cation-exchanged zeolites. The lifetime decreases in a systematic manner as the cation is varied from Li$^{+}$ to Cs$^{+}$ and with decreasing Si/Al ratio and is thus strongly dependent on the basicity of the zeolites. This finding was attributed to the direct interaction between the carbocation and the zeolite host, which may act as a nucleophile, adding to the carbocation to generate a carbocation adduct (framework-bound alkoxy species). The reactive nature of zeolites toward the carbocation, akin to nucleophiles such as water and methanol, was thus revealed.

4. Intracage reactions

In the recent few years, the investigation of photochemical reactions between more than one guest species, e.g. A and B both incorporated in the zeolite, increased significantly, in addition to the photophysical and photochemical studies of individual molecules. Here, we take a look at a few examples and assess the achievements of those studies.

4.1. Excimer and dimer cations

One way to look at intracage reactions is to exploit the heterogeneous distribution of molecules among the cages, e.g. increasing the loading level leads to the multiple occupancy of the cage. Excimer formation of pyrene was investigated as early as 1984 [76] and also later in Na$^+$.X and Na$^+$.Y [66,77,150]. At high loadings, the broad and featureless emission observed at the expense of monomer fluorescence was ascribed to the excimer emission. It was concluded that the excimer emission arises on excitation of dimeric species in doubly occupied cages, since no rise was detected on pulsed excitation in the nanosecond time regime. A concern about pyrene is that crystalline pyrene gives excimer-like emission, and the microcrystals can easily be formed with inappropriate sample preparation procedures. In particular, the use of a rotary evaporator for removing solvent in the early study [76] might have caused the formation of crystals on the outer surface of the zeolites if unadsorbed pyrene were left in solution. Additionally, incomplete isolation of the samples from the atmosphere may lead to subsequent crystallization, as mentioned in Section 2.4. For this reason, the investigation with anthracene or naphthalene is advantageous because the crystals of these species give no excimer-like emission [161].

The excimer emission of anthracene was observed in zeolites Na$^+$.X and Na$^+$.Y by our group [41,74,75]. The observation in the stationary experiment is similar to that of pyrene, but the dynamics characteristic to the zeolites are of interest. The decay rate of the monomer fluorescence is dependent on the loading level: the decay is faster at higher loading levels. On the other hand, the rise in the excimer emission is very fast, on the ps time scale, indicating a significantly fast formation process. One possibility is energy migration from the monomer singlet state to the various configurations or overlapping structures of dimeric species residing in the neighboring cages. The other possibility is to assume a purely dynamic process: fast quenching of the excited singlet state of anthracene by another anthracene occupying the same cage. Since the absorption spectrum of anthracene was not altered depending on the loading level, the formation of a ground-state dimer is not evident in Na$^+$.Y. In contrast, an appreciably deformed absorption spectrum was obtained in channel-type K$^+$.L zeolite, suggesting the formation of the ground-state dimer [75]. Whether the excimer formation is static or dynamic is still not clear for anthracene in Na$^+$.Y.

The excimer emission was observed at high loadings for naphthalene [72,73,75] in Na$^+$.Y and K$^+$.L, and for biphenyl [75] in K$^+$.L. The loading-dependent excitation
spectra clearly suggested that the excimer formation is static for these species in the zeolites. Two noteworthy pictures emerge from the spectroscopic evidence suggesting that the configuration of excimer in Na\textsuperscript{+}-Y should be different from that in K\textsuperscript{+}-L: first, a fully overlapped structure is expected in Na\textsuperscript{+}-Y in contrast to a partially overlapped one in K\textsuperscript{+}-L. Second, the excimer emission of biphenyl observed in highly loaded K\textsuperscript{+}-L was totally unobserved in Na\textsuperscript{+}-Y. In these cases, the matching of pore size and shape with the guest species is considered decisive.

The observation of dimer cations is another example of intracage processes. A study in our laboratory [71,72] revealed the transient absorption spectra of naphthalene to be dramatically dependent on the loading levels in hydrated Na\textsuperscript{+}-X and Na\textsuperscript{+}-Y (Fig. 15).

The hydrated zeolites were employed, because the transient absorption band due to Na\textsuperscript{1+}-Y, which strongly interfere with other bands, can be suppressed. At the low loading level of 1.0 × 10\textsuperscript{-4} mol/g (naphthalene)/[supercage] = 0.017), the transient spectra were obtained that are ascribable to the superposition of triplet state naphthalene, the radical cation of naphthalene (Nap\textsuperscript{•+}) and trapped electrons in the form of both Na\textsuperscript{3+}-L and Na\textsuperscript{2+}-Y (λ∼700–900 nm). At loading level 50 times higher (5.0 × 10\textsuperscript{-4} mol/g), absorption due to the naphthalene radical cations was greatly reduced, and a new broad, featureless absorption band appeared with a peak at 590 nm and a new band also appeared with a λ\textsubscript{max} at 1100 nm. These absorption bands are reminiscent of that of naphthalene dimer cations, which are formed by the association of Nap\textsuperscript{•+} and naphthalene (Nap) in the ground-state: Nap\textsuperscript{•+} + Nap ↔ (Nap)\textsuperscript{2•+}

Dimer cations are characterized by their charge-resonance (CR) absorption band, which corresponds to the transient absorption bands due to Na\textsuperscript{4+} in the form of both Na\textsuperscript{3+}-X and Na\textsuperscript{2+}-Y (Fig. 15).

In the case of Na\textsuperscript{+}-Y in contrast to a partially overlapped one in K\textsuperscript{+}-L. Second, the excimer emission of biphenyl observed in highly loaded K\textsuperscript{+}-L was totally unobserved in Na\textsuperscript{+}-Y. In these cases, the matching of pore size and shape with the guest species is considered decisive.

The formation of dimer cations of other aromatic species within the zeolite Na\textsuperscript{+}-Y has not been demonstrated. This was ascribed to the smaller stabilization energy of the dimer cations of other aromatics compared with that of naphthalene. Very recently, the CR-band of the dimer cations of anthracene (λ\textsubscript{max} = 1500 nm) were observed on excitation of the ground-state dimer formed in K\textsuperscript{+}-L [168]. The result suggests that it is important to hold the dimer pairs very tightly in matrices to stabilize the dimer cations. It is intriguing to generate dimer cations at room temperature utilizing the zeolite framework.

4.2. Electronic energy transfer

Carzaferri’s group devoted themselves to the study of energy transfer and energy migration in dye-doped zeolites, aiming at the construction of artificial antenna systems mimicking chlorophylls [169–173]. They synthesized cylindrical zeolite L crystals ranging in length from 30 nm to 3 μm and incorporated luminescent dyes into the channels of the crystal. A cylinder of 600 nm diameter, for example, consists of about 100,000 parallel-arranged channels. Red-emitting dye molecules (oxonine, Ox\textsuperscript{+}) were put at each end of the channels filled with green emitting dyes (pyronine, Py\textsuperscript{+}). Irradiation of light of appropriate wavelength on the Cylinder caused the absorption only by Py\textsuperscript{+}. The excitation energy then migrates between Py\textsuperscript{+} molecules along the axis.
of the crystal, and is eventually trapped by Ox\(^+\), resulting in the emission of red light from Ox\(^+\). Due to the short distances and the ordering of the electronic transition dipole moments of the dyes with respect to the channels, the excitation energy was considered to be transported by Förster-type energy migration preferentially along the axis of the cylindrical antenna to a specific trap. The main role of zeolite framework is to provide the desired geometry for arranging and stabilizing the incorporated dyes.

Calzaferri’s group investigated this energy transfer system rather extensively\(^{169–173}\). For instance, they investigated the orientation of the \(S_0 \rightarrow S_1\) transition dipole moment of the molecules Py\(^+\) and Ox\(^+\), which have transition dipoles whose orientations are parallel to the molecule’s long axis, incorporated in the channels of zeolite L crystals by means of fluorescence microscopy and single-crystal imaging. The result indicated a cone-shaped orientation distribution of the transition dipole moments with a half-opening angle of 72° around the crystal axis for Ox\(^+\). This in not consistent with the structural model according to which the maximum cone half-angles possible for Py\(^+\) and Ox\(^+\) are 30 and 40°, respectively. The discrepancy between the geometric consideration and the results of the fluorescence measurements was explained by assuming that these species are exposed to a considerable electrostatic field in the zeolite channels. Other topics related to the energy transfer in dye-loaded zeolite L systems can be found in the literature\(^{169–173}\).

Another strategy for realizing an energy transfer-based antenna effect is to exploit rare earth ion-exchanged zeolites, mimicking rare earth chelates\(^{174}\), in which ligands first absorb light, followed by energy transfer to the rare earth ion. As such, the group of García and co-workers attempted to prepare rare-earth complexes of Eu\(^3+\) in which ligands were introduced as the charge-compensating cations with ligands, 2,2′-bipyridine (bpy), benzoitrifluoroacetone (btfa), 1,10-phenanthroline (phen) and dipicolinic acid (dpic) in zeolites, Y, mordenite and ZSM-5\(^{175}\). Formation of the complexes was assessed by various indirect methods. It was found that the complexes formed in the zeolites appeared deficient in the number of ligands compared to those in solution, presumably due to steric constraints from the framework. Upon laser excitation at 266 nm, the zeolites samples exhibited emission at room temperature and the luminescence intensity increased notably upon complexation. The emission decay did not follow simple first-order kinetics, but apparently the luminescence is longer lived. Furthermore, they observed that the nature of the ligand influences the decay of the luminescence. However, no explanation was given for these remarkable observations. They should have looked at the rise of emission to see if they could detect the energy transfer process from the ligands to Eu\(^3+\) and determine the energy transfer rate constant. Also, it is necessary to determine whether the energy transfer is a reversible process or irreversible one, because the emission lifetime of the rare earth ion is affected by the excited-state lifetimes of the ligands, usually triplet state lifetimes if the energy transfer is reversible.

With an idea similar to that of García’s group, Wada et al. made a considerable effort to increase the emission quantum yield of Nd\(^3+\), which rarely emits in fluid media due to the fast relaxation of its excitation energy through non-radiative process and collisions\(^{176}\). They fabricated a complex of Nd\(^3+\) with bis (perfluoroctylsulfonyl)amine as a ligand in zeolite Y. Additionally, they replaced the –OH groups on the surface of the zeolite cages with –OD groups since it was expected that the –OH groups do not have the ability to form a complex with Tb\(^3+\) should induce rapid de-excitation of the excited-state of Nd\(^3+\). A remarkably increased emission quantum yield of about 0.1 was obtained. They attributed the success mainly to the suppression of the relaxation of the excitation energy of Nd\(^3+\) by the low-vibrational zeolite cage wall and the energy migration through collisions by locating Nd\(^3+\) separately in different cages.

More recently, a study from our laboratory\(^{177}\) investigated the energy transfer between guest aromatic species such as benzophenone and naphthalene, and a rare earth charge-compensating cation, Tb\(^3+\), within the zeolites Y and L by the time-resolved measurement of emission from the \(\text{^5}D_4\) excited-state of Tb\(^3+\). Although these molecules do not have the ability to form a complex with Tb\(^3+\) in the
ground-state, a remarkable sensitization of Tb\(^{3+}\) luminescence was observed, presumably due to a supramolecular effect. The observation of the rise and decay of the emission of Tb\(^{3+}\), together with the measurement of triplet decay kinetics enabled the determination of the energy transfer rate constant for the naphthalene/zeolite Y system. The study showed that, while irreversible energy transfer takes place from triplet benzophenone (actually, the protonated form in the zeolite) to Tb\(^{3+}\), reversible energy transfer occurs between triplet-state naphthalene and Tb\(^{3+}\), where the separation between triplet level and the \(1D_0\) level of Tb\(^{3+}\) is small. The remarkable role of the zeolite is ascribed to the enforcement of the formation of a complex between the aromatic species in the excited state and Tb\(^{3+}\). Additionally, in highly loaded zeolite L, the excitonic interaction of Tb\(^{3+}\) was observed in the excited state.

Although not tried so far, sensitization of rare earth emission might be possible via energy transfer upon excitation of the matrix, i.e. the zeolite framework. Such a possibility has already been realized in several other systems. For instance, the energy transfer from an excited matrix to rare earth ions, leading to sensitized emission, has been observed in a Eu\(^{3+}\)-doped silica gel/CdS nanoparticle composite [178], in the two-phase structure of ordered TiO\(_2\) nanoparticles doped with Eu\(^{3+}\) [179], and in Eu\(^{3+}\)-doped thin films of GaN on Si substrates [180], for instance. The literature dealing with these relatively new types of luminescence sensitization of rare earth ions has been surveyed by Calzaferri and co-workers very recently [181].

4.3. Charge transfer and electron transfer

CT and ET have attracted considerable attention due to their practical application for energy storage utilizing charge separation and to the fundamental nature of these reactions in chemistry. Microheterogeneous supports such as zeolites have potential use for aiding the charge separation process by impeding energy waste back-reactions. Aluminosilicate zeolites have shown considerable promise for promoting the stabilization of photochemically generated redox species. The arrangement of cages and channels in these crystalline zeolites allows for the placement of molecules in well-defined, unique spatial arrangements. Here, we examine how zeolites work for CT and ET phenomena.

Adsorption of molecules with electron-donating nature and those with electron-accepting nature within the zeolites has led to the formation of intracage CT complexes due to the attractive force between the donor-acceptor (DA) pairs. The area was pioneered by Yoon et al. by incorporating arene donors into various pyridinium cation-exchanged zeolites [42–45]. Later, the incorporation of a neutral form of both donors and acceptors was found to induce the CT complexes [157,182]. Although zeolites impose restrictions on the size and shape of molecules to be incorporated, the formation of CT complexes inside the cavities is unconstrained by the zeolite framework, and the complexes exhibit properties similar to those formed in solution. For instance, the position of the CT absorption peaks is represented by a linear function of the ionization energy of the donors or the electron affinity of the acceptors, as predicted by Mulliken theory. Nevertheless, the properties of these CT complexes were somewhat affected by various factors: the framework structure, the degree of hydration, and the basic nature of the zeolite.

The excited-state properties of the CT complexes are of considerable interest, because the investigation can be made of the fundamental aspects of photoinduced ET reactions within zeolites. The excitation of the CT complexes of neutral DA pairs normally leads to the CT state (D\(^{+}\)A\(^{-}\)), followed by an ultra-fast charge-recombination (CR) reaction or a back-electron transfer (BET) process [183–186]. Yoon and co-workers observed that the photoexcitation of the MV\(^{2+}\)-arene and other pyridinium–arene CT complexes encapsulated in Y leads to the evolution of a broad transient absorption due to the superposition of the bands of MV\(^{2+}\) and arene \(^{1}A_g\) within the duration (25 ps) of the laser pulse [187,188]. The decay rate (BET process) is at least 10 times slower than that in acetonitrile solution (\(k > 4 \times 10^{10} \text{ s}^{-1}\)). Since the transient absorptions lasted more than 4 ns, they also investigated the behavior on longer time scales with nanosecond laser excitation. The combined picosecond and nanosecond kinetic data establish that there are at least three kinetically distinguishable decay phases of the transients, i.e. one decay process monitored on the picosecond time scale with a lifetime between 45 ps and 1.2 ns, one process monitored on the microsecond time scale with a half-life between 1.6 and 130 \(\mu\)s, and one process with a lifetime greater than 1 ms.

The authors have proposed several factors to rationalize the remarkably long lifetimes of the transients. It is thought that the electrostatic field within the zeolite supercage, as well as the adsorption effects of ionic species at the polar aluminosilicate surface, are factors that contribute to the slowing of the BET. Coulombic interactions between the positively charged transients and the negatively charged framework may explain the incomplete or retarded BET compared with the homogeneous solution. The positively charged transients may be pulled further apart from one another by interacting with the negatively charged framework. Furthermore, the authors think that the negatively charged microenvironment of the zeolite may also influence the reduction and oxidation potentials of the electron acceptor and electron donor, respectively. The CR decays of excited CT complexes consisting of 1,2,4,5-tetracyanobenzene and arene donors [157] were pursued by means of a femtosecond laser photolysis technique. Significantly slower decay kinetics than those in solutions of polar solvents were recorded in the zeolites (Fig. 16).

For the CR decays, the restricted conformational relaxations in the excited-state CT complexes adsorbed in the
zeolites were considered to be responsible for the remarkably slow processes. Thus, two types of mechanisms were proposed for the slow relaxation of the excited CT complexes: either the electrostatic field inside the zeolite or the specific adsorption interaction between the guest species and the adsorption sites in the zeolite. At the present stage, it is difficult to pinpoint which is the predominant factor, because it seems to depend on the chemical nature of both the guest molecules and that of the zeolite.

A laser photolytic investigation of the CT complex between cyclobis-\(N,N'\)-paraquat-\(p\)-phenylene) macrocycle (CV\(^{4+}\)) and 1,4-dimethoxybenzene (DMB), characterized by a broad CT band at \(\lambda_{\text{max}}\) of 475 nm, encapsulated within the supercages of zeolite Y was carried out by García and co-workers [189].

On excitation at 266 nm, the wavelength at which the viologen species embedded in CV\(^{4+}\) mainly absorbs the light and thus away from the location of the CT band, the yield of ET to produce viologen radical cation (CV\(^{3+}\)) decreased dramatically compared with the system containing no DMB. Note here that the excitation of viologens results in the abstraction of electrons from the zeolite host, as mentioned in Section 3.3. In contrast, 532 nm excitation allowed the detection of the CV\(^{3+}\) radical cation and the dimer radical cation of DMB, (DMB)\(_2\)^{2+}, as long-lived transients whose decay was not complete after hundreds of microseconds following laser excitation. The result was considered to indicate that the initially complexed DMB\(^{2+}\) migrates out of the macroring and becomes stabilized by interaction with an electron-rich neutral DMB, forming the dimer cation. Since this was not the case in acetonitrile solution, due to a fast back reaction, these authors considered that the photochemical behavior is distinctive of restricted media. The study demonstrated that stabilizing the product of ET by opening a new pathway is one of the remedies for retarding BET. Note that the photoinduced formation of the dimer cations on excitation of CT complexes was once sought by Yoon and co-workers, but they failed to observe this by exciting CT complexes of arene donors in pyridinium ion-exchanged zeolites [188].

Cozens and co-workers explored ET and charge migration between electron donors and acceptors encapsulated within dry Na\(^+\)-Y zeolites using nanosecond laser photolysis [190]. Photoexcitation of chloranil (Chl) in Na\(^+\)-Y containing co-adsorbed 4,4'-dimethoxybicumene (DMBC) as an electron donor generated the long-lived radical anion (Chl\(^{*-}\)) and 4-methoxycumyl cation, resulting from the decomposition of DMBC\(^{2+}\).
while photoexcitation of trans-anethole (An) in Na\textsuperscript{+}-Y containing co-adsorbed 1,4-dicyanobenzene (DCNB) as an electron acceptor produced An\textsuperscript{•+}, DCNB\textsuperscript{•−} and trapped electrons (e.g. Na\textsuperscript{3+}, Na\textsuperscript{3+}) in zeolites. No evidence for the formation of CT complexes was found in either system. The authors proposed that the fast generation and migration of electrons and holes within the cavities of dry Na\textsuperscript{+}-Y leads to long-lived charge-separated species, rather than the direct redox reactions between donor and acceptor pairs. Note that, in the absence of the quencher, both Chl\textsuperscript{•−} and An\textsuperscript{•+} were produced on photoexcitation by the reaction with the zeolite host, and they are long-lived. The big disadvantage of this exploration is a lack of quenching data to support their proposal, due to the non-emissive nature of the excited states. It should be determined whether or not the singlet and/or triplet excited states indeed react with these quenchers. In this case, a picosecond or femtosecond transient absorption study is needed. An alternative simple explanation for the data is that An\textsuperscript{•+}/DCNB\textsuperscript{•−} pairs are long-lived, because the trapped electrons in dry zeolites are essentially unreactive toward guest aromatic species, as was shown in the previous study \cite{72}, and Chl\textsuperscript{•−} is long-lived, because the oxidized counterpart of the ET, DMBC\textsuperscript{•+} decomposes to a more stable carbocation and radical.

Photoinduced electron transfer (PET) between tris-bipyridyl ruthenium(II) (Ru(bpy)\textsubscript{3}\textsuperscript{2+}, bpy: 2,2'-bipyridine)–bipyridinium acceptors has been extensively investigated as a prototypical system to demonstrate the possibilities for long-term charge separation. Mallouk and Kim demonstrated that PET readily takes place from Ru(bpy)\textsubscript{3}\textsuperscript{2+} on the external surfaces of zeolites (Y, L, and mordenite) to MV\textsuperscript{2+} ions incorporated within the pores \cite{191}. The PET takes more much readily when N,N'-ethylene-2,2'-bipyridinium (2DQ\textsuperscript{2+}) is tethered, as the electron relay, to one of the bpy ligands of the Ru(II) complex and when relay is intercalated into the channels of L incorporating viologen acceptors \cite{192}. The results show that the spatial organization of the photosensitized donor on the external surfaces and corresponding acceptor on the internal surfaces of the zeolite leads to much longer-lived charge separation, as compared to those in which DA pairs are placed in the neighboring cages of Y \cite{193} or in homogeneous solution.

Dutta and co-workers carried out a diffuse reflectance laser photolysis investigation of PET from Ru(bpy)\textsubscript{3}\textsuperscript{2+} synthesized in zeolite Y supercages to various ion-exchanged bipyridinium acceptors (with differing reduction potentials) residing in neighboring supercages \cite{194}. Since the size of Ru(bpy)\textsubscript{3}\textsuperscript{2+} does not allow its exit from the supercage, ET over a distance longer than the separation between adjacent cages (0.5–2 nm, depending on the adsorption sites within the cages and the relative orientations of the molecules) may not be possible during the lifetime of Ru(bpy)\textsubscript{3}\textsuperscript{2+} (0.67 ns). Although the measurement of the rate of forward ET was not possible due to the time resolution of the detection system (lower limit >10\textsuperscript{5}s\textsuperscript{−1}), the rate constants for the BET were measured to be on the order of 10\textsuperscript{4}s\textsuperscript{−1} at wavelengths between 360 and 390 nm, representing the bleaching signal of Ru(bpy)\textsubscript{3}\textsuperscript{2+} and the decay signal of the bipyridinium radical ions due to BET. A significant observation is the formation of long-lived charge-separated species at high loadings of bipyridinium acceptors, and this was ascribed to the presence of a route
for charge propagation by electron hopping via densely packed viologen species to compete with the BET. The ship-in-a-bottle synthesis of Ru(bpy)$_3^{2+}$ in zeolite Y was a very successful example of how nicely the crystalline zeolite allows for placement of molecules in well-defined and unique spatial arrangements within the cages [82,83]. It seems, however, that there still remains room for increased sophistication of the arrangement of molecules within the zeolite, because the experimental observations are still complicated and it is difficult to extract concrete conclusions.

Bossmann et al. demonstrated that TiO$_2$ nanowires incorporated within the interior of Y also serve as an electron relay between the zeolite-encapsulated Ru(bpy)$_3^{2+}$ and a size-excluded Co(III) complex placed in solution [195]. A similar system was investigated by García and co-workers with the transient absorption spectroscopy [196]. Samples of zeolite Y containing 2,4,6-triphenylpyrylium (TPP$^+$) or Ru(bpy)$_3^{2+}$ were prepared, and their photophysical and photochemical properties were compared with the same samples containing encapsulated nanoscopic TiO$_2$ clusters as relays. Upon irradiation of TPP$^+$ and Ru(bpy)$_3^{2+}$ in the presence of TiO$_2$, the transient generation of the pyranyl radical (TPP$^*$) and Ru(bpy)$_3^{2+}$ were observed. These large sensitizers are considered to remain immobilized inside the cavities. Based on a time-resolved fluorescence study, these authors concluded that the quenching of TPP$^*$ or Ru(bpy)$_3^{2+}$ by TiO$_2$ is due to a static mechanism, taking place instantaneously after dye excitation, suggesting that only those excited photosensitizer molecules in direct contact with TiO$_2$ clusters are quenched due to PET from Ru(bpy)$_3^{2+}$ to TiO$_2$ (electron injection) and also from TiO$_2$ to TPP$^+$ (hole injection). Cases of the former type are well known, but those of the latter type are less documented.

Quite recently, Yoon and co-workers reported the PET from Ru(bpy)$_3^{2+}$ encapsulated in K$^+$-exchanged zeolite Y to the size-excluded and externally placed viologen (N$^\prime$-bis(3-dicyclohexylmethyl)oxoaryl-1$^N$-methyl-4,4$^\prime$-bipyridinium [DHC-MV$^{2+}$]) in acetonitrile [197]. Notably, K$^+$ ions were liberated from the zeolite to solution during interfacial ET from Ru(II) complexes to DHC-MV$^{2+}$; they form strong host–guest complexes with added crown ether molecules in solution, which leads to retardation of the reverse flow of cations, and hence, the charge-balancing electrons, from the solution to the zeolite. This is attributed to the photosensitized electron pumping from the zeolite framework to the viologen by the outermost Ru(bpy)$_3^{2+}$ ions. This finding is surprising, because sacrificial electron donors usually necessary for PET in Ru(bpy)$_3^{2+}$-DHC-MV$^{2+}$ pairs are totally absent in the zeolite, suggesting that the zeolite framework serves as an unlimited source of electrons. Several points need to be clarified in this system. First, it is not clear what is the mechanism of electron pumping in the zeolite or which part of the zeolite is responsible for providing electrons to Ru(bpy)$_3^{2+}$ to regenerate Ru(bpy)$_3^{3+}$. Some concerns may be raised that the zeolite framework may undergo decomposition after giving up electrons to compensate for the loss of K$^+$ ions and electrons. Second, in order to explain the highly efficient PET in the zeolite, these authors considered the injection of electrons from Ru(bpy)$_3^{2+}$ to the conduction band of the zeolite, followed by the abstraction of the electrons by DHC-MV$^{2+}$ at the terminus of the framework as an alternative mechanism to the ET between DA pairs in direct contact. If this is the case, Ru(bpy)$_3^{2+}$ should undergo quenching by the zeolite even in the absence of viologen; we suppose that this may not be the case, based on the lifetime data. Zeolites can be regarded as semiconductors, but the exact nature has not been characterized at this moment [198]. Third, although Yoon and co-workers made an amazing observation of thermal ET also taking place from the zeolite framework to DHC-MV$^{2+}$, the exact reducing agent is unidentified. In spite of these ambiguities, Yoon’s group showed that PET in zeolites is highly promising in attaining extremely high yields of charge separation.

The study of ET and related subjects will continue to be an active area of research in zeolite photochemistry, partly from the perspective of promoting charge separation and partly from that of the remaining issues to be solved by research effort.

5. Reactions through intercage migration

Intracage reactions such as exccimer formation, charge- and electron-transfer, and singlet energy transfer, are sufficiently fast processes taking place within the ps and ns time scale. On the contrary, triplet–triplet energy transfer and radical–radical combination in zeolites are very slow and bear peculiar decay kinetics distinct from first- or second-order reactions, because the reactants have to travel through many cages before getting access to a reacting partner, and, more importantly, the distribution of reactants is heterogeneous. These reactions were investigated experimentally and analysis was given to the results based on the theoretical model.

Scaiano et al. [199] examined the quenching of triplet xanthone (Xan) by 1-methylnaphthalene (MeNap) through the triplet energy transfer mechanism in the faujasite Na$^+$-Y, with a diamond lattice structure of supercage networks.
They focused the reaction yields within 100 ns, where the cage-to-cage molecular transport was considered negligible, and thus only quasi-static energy transfer was assumed. In this case, 100 ns was the limitation of the detection system used for the transient absorption measurements. Accordingly, the initial yield of \( \text{Xan}^* \) in the decay curves was observed to decrease with increasing loading level of the quencher, MeNap. Three models were tested for interpreting the variations in triplet yield with quencher concentration: (1) donor and acceptor must share the same cage for the energy transfer to occur; (2) energy transfer can occur in the same cage and in any of its four immediate neighbors (five supercages); and (3) transfer is also possible in second-nearest neighbor cages (for a total of 17 supercages). The experimentally observed yields of \( \text{Xan}^* \) as a function of quencher occupancy, i.e. \([\text{MeNap}]/[\text{supercage}]\) was best fitted by a equation which is based on model 2. Thus, Scaiano et al. concluded that the sphere for energy transfer includes the original excitation supercage and its four nearest-neighbor supercages, but no more.

The study gave some insight into the effective range of triplet-triplet energy transfer, i.e. about 1 nm in the zeolite system. Yet, too simplified a model was used for the description of the energy transfer in such a complicated system. For example, the experimental data points appear to deviate on the side of larger values from the simulated curve as the occupancy of the quenchers increases. Apparently, 100% quenching cannot be achieved at an occupancy of unity, even though the model requires this condition. This is because the model counts the probability of the absence of a quencher in any five supercages, not necessarily the cages consisting of one with the triplet probe and the four immediately neighboring cages. More elaborate analysis based on a sophisticated model is necessary for resolving an interesting phenomenon of energy transfer distance within the zeolite cage networks. Also, the time-dependent decay curves of \( \text{Xan}^* \) should be fully analyzed, which may provide useful information on the mechanistic aspect characteristic to the zeolite, since the assumption of 100 ns for the time limitation to which the quasi-static quenching applies has no solid ground.

Quenching of photoexcited triplet-state anthracene through triplet-triplet energy transfer mechanism by a few energy acceptors, including azulene, ferrocene and also anthracene in the ground-state, was investigated in dehydrated Na\(^+\)-Y zeolite with a diffuse reflectance transient absorption technique by our group [68,200].

At sufficiently the low loading levels of \( \leq 5.0 \times 10^{-6} \text{ mol/g} \), the decay of triplet-state anthracene was approximated by a single exponential function with a decay constant of \( 54 \pm 5 \text{ s}^{-1} \). Upon addition of the quenchers, dynamic quenching of triplet-state anthracene was observed. A faster decay was observed with increasing loading level of quenchers, and the decay curves were non-exponential (Fig. 17).

The probe molecules are expected to either self-deactivate or undergo quenching through collision with another doped species (a quencher) continuously migrating within the cage networks, since the triplet-triplet energy transfer proceeds mainly through a collisional mechanism due to exchange interaction [201]. The general method of time-resolved diffusion-mediated excited-state deactivation has already found application for probing dynamical and structural properties of a variety of microheterogeneous media, such as colloids [67]. The kinetics of the excited-state quenching in zeolites are most conveniently described in terms of the CTRW model [202–204]. In its simplest but still quite realistic formulation, it assumes that quenchers perform independent random walks that involve unbiased jumps to nearest-neighbor lattice sites, and the waiting time distribution function in each site is exponential. The lattice site is normally associated with a zeolite supercage, but generalization to true adsorption sites is possible. Supercages are assumed to be occupied by reactants at random, according to the Poisson law. The reaction is assumed to take place whenever the probe and the quencher are in the same supercage. For open zeolite structures, quenching may also occur when the probe and the quencher reside in neighboring supercages, as was pointed out by Scaiano et al. [199].

The final expression for the experimentally observable excited-state survival probability \( \Phi(t) \) is given by [200]

\[
-\ln \Phi(t) = k_0 t + \tilde{n} R(t),
\]

where \( k_0 \) is the excited-state self-decay lifetime, \( \tilde{n} \) is the average number of quenchers per supercage \([\text{quencher}]/[\text{supercage}]\), typically, \( \tilde{n} \ll 1 \), and \( R(t) \) is the time-dependent reaction flux. The analytical expression for \( R(t) \) includes \( k_p \), the pseudo-first-order rate constant for the intracage quenching; \( k_{\text{ex}} \), the rate constant for the intercage migration; and \( k_{\text{q}} \), the rate constant for quenching from the neighboring supercage (Fig. 18).

It follows from Eq. (1) that the function

\[
F(t) = -R(t) = \frac{1}{\ln \Phi(t)} [\ln \Phi(t) + k_0 t]
\]

must be universal for any quencher concentration, as long as low quencher concentrations are employed (\( \tilde{n} \ll 1 \)).
be thought of as the decay function in the presence of just one quencher and in the absence of self-deactivation. Eq. (3) was used as a test of the applicability of the present treatment to the experiments. Fig. 19a and b shows the plots according to Eq. (3), universal plots for two quenching systems, azulene and ground-state anthracene, in dehydrated Na\textsuperscript{+}-Y zeolite.

The experimentally observed universality suggests that the CTRW model is applicable to the quenching of triplet-state anthracene.

Two significant findings were obtained from this triplet quenching study. First, self-diffusion coefficients were extracted from the cage-to-cage migration rate constant, \(k_\text{cc}\), for the large aromatic molecules, anthracene, azulene, and ferrocene in dehydrated Na\textsuperscript{+}-Y. The very small values, ranging from \(10^{-15}\) to \(10^{-18}\) m\(^2\)/s at room temperature, cannot be measured by traditional techniques, i.e. PFG NMR and QENS. Thus, the triplet quenching method, which probes longer time scales (ns to 100 ms), can be complementary to other established techniques in zeolite science. Second, by the analysis of the experimental decay curves based on the CTRW model, the detailed reaction mechanism was revealed to depend on the zeolite lattice topology as well as on the dynamics of migration of guest molecules between adsorption sites. In dehydrated Na\textsuperscript{+}-Y zeolite, where connecting windows are wide and the distance between adsorption sites in the neighboring cages is small enough to allow sufficient overlap of the wave-functions, the probe can be deactivated by quenchers residing not only in the same cage but also in the four cages of the first coordination sphere (see Fig. 20).

Interestingly, in hydrated zeolites, where co-adsorbed water molecules are expected to block the interconnecting windows between the cages, quenching from neighboring cages is not possible. In future work, a temperature study might be needed, because the activation energy of diffusion can be obtained, the value of which might be discussed in comparison with that of the extensively studied benzene. Additionally, the validity of the order of the diffusion coefficients obtained should be checked by other methods.

Johnston et al. reported an experimental and theoretical study of the recombination of diphenylmethyl radicals generated by flash photolysis of the precursors, 1,1,3,3-tetraphenylacetone and 1,1-diphenylacetone in Na\textsuperscript{+}-X zeolite [205]. The diphenylmethyl radical concentration, monitored by time-resolved diffuse reflectance spectroscopy, decreased roughly linearly with the logarithm of time, indicative of a reaction rate that decreases gradually. The overall decay pattern depended only weakly on temperature, precursor, or laser dose. For the first time, they applied a method based on the random walk concept to the diffusive motion of the radicals in the zeolite lattice, a diamond structure of the linked cavities. The dominant
decay mechanism is geminate recombination, as evidenced by product analysis. For short times (200 ns–10 μs) and low precursor concentrations, the rate of geminate recombination generated by the model yielded a satisfactory reproduction of the observed time dependence. However, for long times, the fraction of radicals surviving geminate recombination falls well below the theoretical limit of 51%. They reasoned that quenching processes other than non-geminate recombination are responsible for this behavior, although they did not suggest the exact mechanism. We suggest that, due to the high polarity of the zeolite medium and an appreciable absorption of 266 nm light by the host zeolite, photoionization of both the precursors and Na\(^{+}\)-Y zeolite can produce radical cations and trapped electrons, which may interfere with the detection of the radicals [206]. Nevertheless, their mathematical treatment is rigorous and constitutes a prototype for theoretical analysis in reactions involving interchange migration of molecules.

Cozens et al. reported the first detection of benzyl radicals by the transient diffuse reflectance spectrum generated upon 266 nm laser excitation of phenylacetic acid incorporated in dry Na\(^{+}\)-Y [207]. Laser photolysis of dibenzyl ketone, usually used in solution studies to generate the radical, was not successful in Na\(^{+}\)-Y for the observation of the radical, hampered by other unknown transient species. Although detailed analysis was not carried out on the decay kinetics, the decay of the benzyl radical is non-exponential, ranging from μs to ms and also depends on the charge-compensating cations: the decay is faster in the order Li\(^{+}\)-Y > Na\(^{+}\)-Y > K\(^{+}\)-Y > Rb\(^{+}\)-Y > Cs\(^{+}\)-Y. The explanation is given that the benzyl radical essentially decays by a coupling reaction with a second benzyl radical, and the mobility decreases along the series from Li\(^{+}\)-Y to Cs\(^{+}\)-Y; yet, some portion of the radicals generated decays very slowly, because they are generated within local domains, where diffusion is restricted. It might be interesting if the decay kinetics of the benzyl radical are analyzed in terms of the CTRW model [68,200] because we can have a better picture of the diffusional motion of the radicals in the lattice.

The elucidation of the kinetics and mechanisms of reactions involving intercage migration of adsorbed species is important for catalytic and synthetic applications of zeolites. More research effort is needed from both the experimental and theoretical points of view, to accumulate basic data such as diffusivity and reaction yields, which are beneficial to people who want to use zeolites for practical applications.

6. Summary

We have shown an overview of the research activities in photochemical studies of organic molecules adsorbed in zeolites carried out over the past 10–15 years, mainly with transient spectroscopic techniques. Transient spectroscopic studies in zeolites, with their structural integrity and tunable chemical properties have brought to light a great deal of use-
ful information on the excited-state behavior of molecules, in particular, dynamic processes mechanistically different from those in homogeneous solutions. This approach has helped to clarify the zeolite medium considerably from the photochemical point of view and has made a certain impact on the zeolite science community in terms of the types of information obtainable by various experimental techniques. Research efforts utilizing zeolites as host materials also have indicated the way of controlling the photochemistry of adsorbed guest species. Many examples of such cases dealing with the “control of photocatalysis” were given as well as those dealing with the “control of photochemical reaction pathways”. Thus, the interplay with zeolites will continue to be of great benefit to the photochemistry community. From the viewpoint of methodology, transient spectroscopy with a diffuse reflectance detection technique still has experimental limitations and technical issues to be overcome for providing experimental data with reliability similar to that of transmittance mode spectroscopy, despite the increasing popularity. Additionally, developing theoretical treatments that describe complex kinetic behavior of excited species within zeolites on the basis of a simplified picture are very important. Given the efforts being carried out from both experimental and theoretical standpoints, we will see further developments in this area in the next few years.

Acknowledgements

We are grateful to the following sources of financial support: the Izumi Science and Technology Foundation (grant no. H13-J-62), the Iketani Science and Technology Foundation (grant no. 011023-A), the Japanese Ministry of Education, Culture, Sports, Science and Technology (Grant-in-Aid for Scientific Research, Priority Area 417, #14050100), and the Japan Society for the Promotion of Science (Grant-in-Aid for Scientific Research #14550796).

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