Long-lived electron–hole pair formation through photoionization of diphenylacetylene occluded in medium pores of aluminum rich $M_{6.6}$ZSM-5 zeolite (M = Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$)
Influence of the counterbalancing cations on the recombination rate

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ABSTRACT

Diffuse reflectance UV–vis and Raman spectroscopies show complete sorption of neutral diphenylacetylene (DPA) in the void space of $M_{6.6}$ZSM-5 zeolites (M = Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$) after several months of exposure of solid DPA to empty zeolite at room temperature. After a long organization period, the laser photolysis of DPA occluded in $M_{6.6}$ZSM-5 generates long-lived DPA$^{•+}$ radical cation as primary phenomenon. Charge recombination occurs mainly through electron transfer and DPA@$M_{6.6}$ZSM-5$^{•-•+}$ electron–hole pair formation. This subsequent electron transfer takes place between the electron deficient radical cation DPA$^{•+}$ and the electron donor oxygen atom of zeolite framework. The multivariate curve resolution analysis of the DRUVv spectra recorded during the reaction sequence including charge separation, electron transfer and charge recombination provide the specific absorption spectra and respective spectral concentrations of all species as function of time. The DRUVv spectrum assigned to the long-lived DPA@$M_{6.6}$ZSM-5$^{•-•+}$ electron–hole pair exhibits broad bands between 450 and 550 nm. The electron–hole pair recombination depends on M$^+$ and appears to be in relation with the electron donor properties of the framework. The charge recombination rate decreases in the order Cs$^+$ > Rb$^+ \sim$ K$^+$ > Na$^+$ > Li$^+$. The electron–hole pair lifetime exceeds several hours at room temperature. The stabilization of DPA$^{•+}$-electron pair and DPA@$M_{6.6}$ZSM-5$^{•-•+}$ electron–hole pair depends on the combined effects of confinement which dramatically reduces the DPA mobility in the zeolite void space and on the intrazeolithe electrostatic field of DPA@M_nZSM-5 (M = Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$).

1. Introduction

Diphenylacetylene (DPA) is a molecule of primary importance because it represents the structural unit of the phenylene acetylene oligomers that are involved in many applications. Because of their good rigidity and conductivity, DPA derivatives constitute a wide range of compounds that present a great potential for many applications in the field of molecular electronic devices. DPA can be used as a model to investigate and to understand the electron and charge transfers in all DPA based oligomers. They can act as molecular switches [1], molecular memory devices [2,3] and digital computers [4]. Some DPA oligomers are also considered as ideal prototypes for molecular wires [5] and can be incorporated into liquid crystalline compounds also to improve the optical behavior of the materials [6].

The development of macromolecular systems that are capable of generating a long-lived generated state is of particular interest for technological advances in solar energy conversion and molecular devices. In simple molecular dyads that demonstrate rapid rates of charge separation, the efficient generation of the photocurrent has not been yet achieved because of too fast charge recombination after photoirradiation [7,8]. Therefore, to generate a long-lived charge separated state, the charge recombination must be slowed down by spatially separating positive and negative charges. As predicted from the electron transfer theory, the rates of charge recombination between the electron donor and acceptor are dependent upon the energetics and in particularly of the driving forces of the process [9]. In this context, the dynamics of charge separation and charge recombination in synthetic DNA hairpins in which DPA organic chromophores are used as linkers have been investigated [10,11]. Hence, the core function of the reaction is a sequence of photoinduced energy and electron transfers between donors and

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acceptors in the antenna complexes and the reaction center. Among various systems nanoporous aluminosilicate materials like zeolites are of particular importance for the construction of models. They constitute organized host guest systems materials in which the host imposes a specific spatial organization to selected active molecules and because of high polarization and high confinement effect, such environment might induce spontaneous ionization of low ionization potential molecules. Zeolites have shown high potential for stabilizing charge separation states spontaneously created or photoinduced [12–21].

Among zeolites, ZSM-5 are crystalline aluminosilicates possessing an open framework of molecular-sized straight and zigzag channels. Rod-shape molecules like polyaromatic hydrocarbon or diphenyl polyene were reported to enter through the straight channels and to exhibit close match with the pore size [22–26]. Due to the presence of trivalent aluminum in the framework, the net charge of aluminum is negative and must be counterbalanced by a cation. Nevertheless, the M^+ cations do not only act as simple charge compensating species but also affect drastically the electron donor strength of the zeolite framework and therefore the stabilization of charge separated states. The double role of electron acceptor and electron donor of the zeolite framework was already observed as well after sorption and subsequent photoionization of rod-shaped molecules as after spontaneous ionization [27–31]. Furthermore, it was established previously not only within narrow pore ZSM-5 [32–35] but also within the larger cavity Y zeolite [18] that the nature of the extra framework cation affects significantly the distance of electron migration within the framework and therefore the lifetime of charge separated states. Consequently, according to zeolite properties and because DPA stands for the structural unit of the conjugated oligomers and can provide a good model for investigating the structural and electronic properties that control the electron transport in phenylene acetylene oligomers, in the present work we seek to study the effect of the zeolite void space on charge separated state created by photoexcitation of previously occluded DPA. First, we employ diffuse reflectance UV–vis absorption (DRUVv) and Raman scattering spectroscopies to monitor the course of DPA sorption in aluminum rich $M_{6.6}$ZSM-5 zeolites for various alkali extraframework cations (M = Li^+, Na^+, K^+, Rb^+, Cs^+), under dry and inert atmosphere without any solvent. The conformations and sorption sites of occluded DPA are predicted using Monte Carlo simulations and subsequent molecular mechanics calculations. This modeling study is expected to support the structural interpretation of the spectroscopic results. After laser photolysis, the fate of the photoinduced DPA$^{•+}$-electron pair is explored over several days. Multivariate chemometric methods are used to resolve the UV–vis absorption spectra and spectral concentrations of pure species involved in the ionization, electron transfer and charge recombination course. The lifetimes of DPA$^{•+}$-electron moiety and subsequent electron–hole pair are obtained by data processing.

2. Experimental

2.1. Materials

As-synthesized $Na_{6.6}$ZSM-5 samples (Si/Al = 13.5, average particle size 1 μm) were obtained according to the template procedure in alkaline medium from VAW aluminum (Schwandorf, Germany). Crystals of silicalite-1 (Si/Al > 1000, average particle size 2 μm) were synthesized in high purity according to the fluoride medium procedure in the "Laboratoire des Matériaux à Porosité Contrôlée", UMR-CNRS 7016, Mulhouse, France. The as-synthesized ZSM-5 zeolites were calcined under air to evacuate the template. The extra framework cations were completely exchanged by Li^+, K^+, Rb^+, Cs^+.

The exchange was carried out according to the processes reported previously [36]. All the bare zeolite samples were dehydrated by a calcination procedure up to 773 K under argon. The chemical analyses, powder XRD patterns, ^{29}Si, ^{27}Al MAS-NMR, IR, Raman, DRUVv, and EPR spectra of $Na_{6.6}$ZSM-5 sample were found to be characteristic of well-crystallized porous compound with following formulae per unit cell: $M_{6.6}(AlO_2)_{6.6}(SiO_2)_{89.4}$. Particularly, no evidence was found for Brønsted acidic sites using IR absorption spectrometry and pyridine absorption.

Diphenylacetylene (DPA 99% $C_{14}H_{10}$, ACROS Organics) was purified by sublimation and stocked over molecular sieves. Pure and dry Ar gas was used.

2.2. DPA sorption in M_nZSM-5

Weighed amounts (∼1.4 g) of powdered hydrated zeolite $M_n(AlO_2)_n(SiO_2)_{96-n}$ were introduced into an evacuable heatable silica cell. The sample was heated up to 773 K under Ar. Then, the sample was cooled to room temperature under dry argon. Weighed amounts of DPA corresponding to 1 DPA/UC were introduced into the cell under dry argon and the powder mixture was shaken. The powders were transferred under dry argon in a quartz glass Suprasil cell for Raman and DRUVv experiments. The powder mixtures were left at room temperature. The loaded DPA@$M_{6.6}(AlO_2)_{6.6}(SiO_2)_{89.4}$ samples were studied and irradiated after complete sorption and equilibration.

2.3. Molecular modeling

The molecular modeling of the DPA preferred sorption sites in $M_n(AlO_2)_n(SiO_2)_{96-n}$ zeolites was performed using Material Studio Modeling package (version 4.4) from *Accelrys International*. The structural parameters and partial atomic charges of silicalite-1 with $(SiO_2)_{96}$ unit cell were taken from previous work [37]. The M_6ZSM-5 structural model was built from the location of Al framework atoms deduced from the Cs^+ location in several series of Cs-exchanged MFI phases determined at several Si/Al ratios [38–42]. The structural parameters and set of partial atomic charges of DPA were derived from previous structural and theoretical works [43–45]. The non-bonding Lennard–Jones (L–J) force field values were taken from previous works [37,46]. The simulation box consists of 2 × 2 × 4 orthorhombic cells. In the Monte Carlo (MC) calculations, the Si, Al, O and M^+ (M = Li^+, Na^+, K^+, Rb^+, Cs^+) positions were fixed in the simulation box. Periodic boundary conditions were applied in all directions. The DPA structure was taken to be rigid.

The MC simulations at 1 DPA/UC loading were carried out at 300 K using the conventional Metropolis algorithm taking into account the non-bonding interactions (E_{ZS}) between the O and M^+ atoms of zeolite and the C and H atoms of DPA as well as the non-bonding interactions (E_{SS}) between DPA. The interactions inside the zeolite were modeled by L–J and coulombic forces.

$$E_{ZS} + E_{SS} = \frac{A_{\alpha\beta}}{r_{ij}^{12}} - \frac{B_{\alpha\beta}}{r_{ij}^{6}} + \frac{q_i q_j}{r_{ij}} \qquad (1)$$

A cut-off radius of 0.9 nm was applied to the L–J interactions. The long-range electrostatic interactions were calculated using the Ewald summation method. The simulation takes a number of steps to equilibrate from its original random position. From each sorption trajectory, a histogram of the energy distribution for sorbate was generated. In a so-called mass-cloud analysis the center of mass of DPA in each configuration was displayed as a dot in the model space. In the molecular mechanics (MM) simulations the time consuming Ewald summation has not been used. The zeolite framework was taken to be fixed and the M^+ extraframework cations and DPA