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Photoinduced electron transfers after t-stilbene incorporation in zeolite. Effect of the presence of an electron acceptor on the reactivity

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ABSTRACT

Diffuse reflectance UV–vis absorption and EPR spectroscopies are used to study photoinduced electron transfers in supramolecular assemblies composed of donor (t-stilbene, t-St) and acceptor (dicyanobenzene, DCB) guest molecules incorporated in MFI zeolites. By using Al-free silicalite-1, it clearly appears that the presence of the acceptor has no effect on the reactivity and that no electron transfer occurs to DCB after t-St photoionization and radical cation ($\text{t-St}^{\bullet +}$) formation. On the contrary, we show evidence for the striking slowing down of the recombination reaction in the presence of the acceptor molecule in the channels of MZSM-5 ($M = Na^+, Cs^+$). In these Al-rich zeolites, electron transfers are mediated by the framework which does not remain passive after photoexcitation. Indeed, zeolite acts both as an electron acceptor and as an electron donor and strongly influences the reaction mechanisms. The donor character is put forward to explain the indirect recombination of the radical cation to form an electron/hole pair. Concerning the acceptor ability of zeolite, we show that the attracting and stabilizing character of NaZSM-5 competes with the acceptor property of dicyanobenzene and then, does not allow total electron transfer to the guest. Even if the $\text{DCB}^{\bullet -}$ radical anion formation does not occur, HYSCORE experiments show strong electron density in the surrounding of DCB indicating partial electron transfer and explaining the trapping of electron and the slowing down of the charge recombination.

1. Introduction

The internal volume of zeolites is well known for accommodating molecules or polymers with dimensions similar to their pore opening sizes and then, can provide a specific environment which can give rise to supramolecular chemical reactivity of high interest. In particular, the photochemical behavior can be sufficiently affected to lead to unexpected and original reactivity associated with promising researches. In this context, numerous studies provide evidence for the real ability of these materials to play a crucial role for light-driven chemistry and possibly for allowing the achievement of efficient artificial light harvesting systems [1–6].

Indeed, the role of zeolites in photoinduced electron transfers was found to be determinant for stabilizing charge separated species [7–20]. The formation and persistence of such long-lived charge separated states was notably explained by the presence of a high internal polarizing electrostatic field and by the confinement effect [21,22]. In addition, due to the presence of basic and acidic Lewis sites in the structure, the electron acceptor and electron donor properties of the zeolite framework were put forward to explain the electron transfer processes occurring after photoionization of a donor molecule incorporated in the zeolite microporous volume [8,10–16]. These electron transfers within the cages and the channels can be mediated by the framework. Especially, the electrons and positive electronic holes can migrate over distances exceeding 10 Å by charge hopping [5,12,23].

The aluminium content and the extraframework cation type were also found to be essential factors to facilitate the charge trapping and/or migration. However, even if the involvement of the zeolite framework in the electron transfers is now clearly demonstrated, various behaviors were reported in terms of transient species lifetimes and of reaction pathways after the guest molecule ionization depending on the zeolite morphology and on the nature and size of the cation. Then, reaction mechanisms are not only narrowly related to the electronic properties of the guests but also of the zeolite host. Consequently, the objective of this study is to investigate electron transfers in supramolecular assemblies where both the incorporated molecules and the zeolite can act as electron donor and as acceptor. The acceptor property of the zeolite has

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often been observed by the trapping of ejected electron in the framework occurring after ionization of occluded molecules and radical cation formation [8,10–16,22,24,25]. The electron donating ability of the host was initially described after photoexcitation of zeolites containing strong electron acceptors such as 1,2,4,5-tetracyanobenzene [26,27] or methylviologen dication [28,29] and also upon channel-type zeolite ability of releasing electron to form positive electronic hole leading to electron/hole pair [22,24,25,30]. Thus, after co-adsorption of an electron donor (t-stilbene; I.E. = 7.8 eV) [21,22,31,32] and of an acceptor (dicyanobenzene) [33,34] molecules within the channels of three MFI type zeolites (silicalite-1; MZSM-5 with M = Na^+, Cs^+), we report the electron transfers following the photoexcitation of the sample. The characterization and interpretation of the reaction mechanisms are carried out by direct comparison with the data previously reported for t-stilbene [21,22,31] and for dicyanobenzene incorporated as unique species in similar zeolites. Especially, we show evidence for the striking slowing down of the recombination reaction in the presence of the acceptor molecule in the channels of ZSM-5.

2. Experimental section

2.1. Material

NaZSM-5 samples (Si/Al = 13.5; average particle size ~1 μm) were obtained from VAW aluminum (Schwandorf, Germany). CsZSM-5 samples were prepared by exchanging the initial sodium extraframework cation by Cs^+ using CsCl chloride salts. First, the exchange process is carried out by suspending zeolite powder in CsCl aqueous solution under stirring. After 24 h, the solid phase is filtered off and dried at 200 °C in an oven for 12 h, then stirred again with a fresh solution of chloride salt, and then dried. The procedure is repeated 4 times. The resulting solid is washed by deionized water, isolated, dried at 200 °C for 12 h, and then calcined at 450 °C in ambient air for 6 h. The purely siliceous MFI (silicalite-1) sample synthesized in fluoride medium was a gift from Dr Patarin (Institut de Sciences des Matériaux de Mulhouse UMR CNRS 7228, France). *t*-stilbene (t-St, $C_{14}H_{12}$ Merck-Schuchardt) and 1,4-dicyanobenzene (DCB, $C_8H_4N_2$ Sigma Aldrich) were purified by sublimation. Pure and dry Ar gas was used.

2.2. Sorption procedure

Weighed amounts (~1.4 g) of zeolite were introduced into an evacuable, heatable silica cell placed in a vertical oven connected to a piping network. The sample was heated stepwise up to 450 °C under flowing dry Ar for 12 h. Then, the sample was cooled to room temperature under dry argon. Weighed amounts of guest molecules corresponding to 0.5 molecule per unit cell (UC) were introduced into the cell without any solvent under dry Ar and then the powder mixture was shaken. After homogeneous mixing the powder was transferred under dry argon in a quartz glass Suprasil cell and sealed. The sorption takes place by sublimation via slow diffusion of the molecules into the zeolite channels. The duration of the sorption process depends on the molecule dimensions and on the zeolite structure and composition. Within Al-rich MZSM-5, the guest molecules need to find sorption sites of lower energy in the proximity of extraframework cations [22] and consequently, the diffusion process is significantly slower than in Al-free silicalite-1. During the sorption process, the intensity of the absorption bands of the guest molecules increase progressively in the UV spectral range and the sorption is assumed to be completed when the spectra did not evolve anymore.

2.3. Diffuse reflectance UV–visible (DRUVv) absorption spectroscopy

The UV–visible absorption spectra of the samples were recorded using a Cary 6000 spectrometer. The instrument was equipped with an integrating sphere to study the diffuse reflectance of powdered samples stocked under an inert atmosphere in quartz cells; the corresponding bare zeolite was used as the reference. The spectra were plotted as the Kubelka-Munk function.

2.4. Raman spectroscopy

A Bruker RFS 100/S instrument was used as a near-IR FT-Raman spectrometer with a CW Nd:YAG laser ($\lambda_0 = 1064$ nm) as excitation source. A laser power of 100–200 mW was used. The spectra of samples stocked under argon in the quartz cells were recorded in the region 3500-150 cm^{-1} with a 2 cm^{-1} resolution using 600 scans. Note that such experimental conditions do not alter the sample integrity. After sorption of the guest molecules, the samples corresponding to neutral molecules incorporated in preferred sorption sites are very stable and do not evolve under the laser beam. No thermal effect and no photoinduced process occur.

2.5. Time-resolved diffuse reflectance UV–visible (TRDRUV) absorption spectroscopy

The experimental set-up for nanosecond diffuse reflectance spectroscopy was previously described [35]. Excitation pulses at 266 nm (7–8 ns, 1.5 mJ) were delivered by a 20-Hz Nd:YAG laser (DIVA II, Thales laser). The probe light was provided by a Xe lamp (XBO 150 W/CR OFR, OSRAM). A UV filter was used to avoid photochemical reactions by the analyzing light. The reflected light was dispersed by a monochromator (Horiba Jobin-Yvon, iHR320) and analyzed with a photomultiplier (R1477-06, Hamamatsu) coupled to a digital oscilloscope (LeCroy 454, 500 MHz). For these powder samples, the transient absorption intensity is displayed as percentage absorption (% absorption), given by % absorption = 100 × ($1-R/R_0$), where $R(\lambda,t)$ and $R_0(\lambda,t)$ represent the intensity of the diffuse reflected white-light probe with and without excitation, respectively. Kinetic traces from 3 μs to 500 μs were detected in the 300–700 nm spectral domains every 5 nm from which transient spectra were reconstructed. To maintain sample integrity during the experiment, the sample was moved and/or shaken throughout the experience to ensure that a fresh region of the sample was probed by each laser pulse.

2.6. EPR

The CW X-band EPR spectra of the powders were obtained as a function of time by using a Bruker ELEXYS 580-FT spectrometer. The EPR spectra were double integrated using Bruker software.

The hyperfine sublevel correlation spectroscopy (2D-HYSCORE) measurements were carried out at 5 K using a Bruker cryofree cryostat system. The 2D-HYSCORE spectra was recorded with the following pulse scheme, $\pi/2$- τ - $\pi/2$-t_1- π -t_2- $\pi/2$- τ echo, and a four-step phase cycle where the echo is measured as a function of t_1 and t_2 with t_1 and t_2 being incremented by steps of 16 ns from their initial value. The pulse lengths of the $\pi/2$ and π pulses in these experiments were 16 and 32 ns, respectively. Prior to Fourier transformation of the HYSCORE data the background decay was removed using a polynomial fit and apodized with a Hamming function.