filtered, and the volatile components were removed in vacuo. The residue was isolated by means of column chromatography (SiO_2, dichloromethane:hexane 1:1 – 10:1) and characterized by means of ^1H and ^{13}C NMR spectroscopy as well as by GC/MS and HRMS.

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Electron-Hole Pairs Stabilized in Al-ZSM-5 Zeolites**

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Photoinduced electron transfer to yield charged-separated states is the most fundamental energy conversion process of the photovoltaic effect, exciton storage in semiconductors, and photosynthesis. Ionization of organic molecules on heterogeneous catalysts[1, 2] is predicted to become an exciting area of research. However, practical applications are often hampered by a rapid back reaction. Inhibition of the undesirable back-transfer of electrons requires control of both electronic and spatial properties of the system. Photoinduced charge separation can be achieved by sophisticated molecular triads and higher analogues that are currently capable of producing a charge-separated state with good yield and a lifetime of less than 1 s.[3] Microporous aluminosilicate materials such as zeolites provide an appropriate microenvironment to efficiently trap electrons.[4, 5] The electron trapped in zeolites can be generated in different ways: 1) radiolysis using high-energy radiations, 2) photolysis of preadsorbed molecules, and 3) mere exposure of electron-donor compounds such as alkali metal vapor or organic compounds to dehydrated zeolites. It appears that the presence of heteroatoms such as aluminum in the siliceous framework and extra-framework cations is a requirement for efficient electron trapping.[6, 7] Although the characterization of occluded organic radical ions has been established, the whereabouts of electrons within the inorganic supports remains unclear and is the subject of considerable debate.[1, 2, 4, 5, 8] Surprisingly, aluminosilicate zeolites are also known to contain electron-donor sites capable of transferring electrons to strong acceptors. Herein, we characterize the unusual system of acidic Al-ZSM-5 zeolite loaded with biphenyl (BP, $C_{12}H_{10}$) groups in which both electron-acceptor

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and electron-donor capabilities of the zeolite are used to generate and stabilize ultrastable electron-hole pairs.

After removal of the template and water molecules from the framework of the as-synthesized ZSM-5 zeolites by a calcination procedure, the framework topology of ZSM-5, $H_n(AlO_2)_n(SiO_2)_{96-n}$, comprises a three-dimensional network of straight and sinusoidal channels.[9] Brønsted acid sites were assigned to the bridging OH group of the Si-OH-Al moieties, and the Al atoms were assumed to be randomly substituted by Si. Special attention was paid to the purity of the as-synthesized zeolites as well as to the dehydrated bare acidic samples, even beyond impurity levels normally detected by conventional elementary analyses.[10] After calcination of as-synthesized zeolites at 800 K under O_2 and subsequent rehydration, no extra-framework aluminum species were detected by ^{27}Al MAS-NMR spectroscopy for hydrated H_nZSM-5 samples containing less than four Al atoms per unit cell. After another dehydration procedure under vacuum or argon or O_2 at 800 K and subsequent evacuation under vacuum, all the physicochemical measurements (powder X-ray diffraction, ^{29}Si MAS-NMR, EPR, Raman, UV/Vis, and IR absorption) provide clear evidence of pure bare ZSM-5 zeolites. In particular, no EPR signal corresponding to iron(III) ($g = 4.26$) or other paramagnetic impurities was detected in the spectra of the samples before exposure to biphenyl (BP).[11] It should be noted that after the calcination procedure at 800 K under O_2, the sharp bands assigned to the OH stretching mode of the Al-OH-Si unit broaden significantly with respect to those of an identical sample calcined under argon at the same temperature.

In the dark, BP molecules were sorbed as intact molecules as BP/H_nZSM-5 through exposure of weighted amounts of BP under argon to H_nZSM-5 samples dehydrated under vacuum or argon. In contrast, spontaneous partial ionization of BP occurs when H_nZSM-5 was calcined under O_2. This striking phenomenon was detailed previously and used below.[10, 12] The rod-shaped BP molecule can penetrate and self-assemble in the pores of the zeolite. In its energetically favorable site, BP lies in the straight channel in a twisted conformation, and diffusion was found to be slow at room temperature.[13]

Laser photolysis of BP/M_nZSM-5 was investigated previously by transient absorption and time-resolved resonance-Raman spectroscopy on the nanosecond time scale.[7] The photoionization generates primarily the biphenyl radical cation $BP^{\bullet+}$ and a trapped electron, abbreviated as ZSM-$5^{\bullet-}$. Then, the electron-deficient $BP^{\bullet+}$ captures another electron from the zeolite framework and regenerates neutral BP(S_0) in the ground state which leads to a so-called electron-hole pair, denoted as BP/M_6ZSM-$5^{\bullet-\bullet+}$.[7] No evidence was found for BP as an electron scavenger through the detection of the biphenyl radical anion $BP^{\bullet-}$. The lifetimes of these transient species increase dramatically as the aluminum content of the ZSM-5 framework increases and were found to depend highly on the nature of the extra-framework cations M.[7] After the disappearance of the $BP^{\bullet+}$ and the regeneration of occluded BP(S_0), the electron-hole was found to persist for one day at room temperature for high aluminum content and suitable extra-framework metal cations.[7]

The presence of a proton as the counterbalancing cation in H_nZSM-5 induced unusual behavior with regard to the formation and stabilization of electron-hole pairs from occluded BP.[10, 13] The photolysis of BP/H_nZSM-5 zeolites under argon generates $BP^{\bullet+}$/H_nZSM-$5^{\bullet-}$ and then finally the ultralong electron-hole pair BP/ZSM-$5^{\bullet-\bullet+}$. Analogous stable electron-hole pairs were also obtained thermally through the mere exposure of BP under argon to H_nZSM-5 obtained from calcination at 800 K under O_2 and subsequent evacuation under vacuum. Introduction of BP (one BP molecule per unit cell loading) turned the powder from white to blue and after one week the solids turned pink. Complete disappearance of $BP^{\bullet+}$ and self-organization of the system required approximately one month. The samples obtained by the photochemical and thermal processes exhibit identical physicochemical characteristics; however, the thermal process allowed a better control of the unpaired electron density as well as a better homogeneity of the samples.

After the complete disappearance of the Raman bands of $BP^{\bullet+}$, all the characteristic Raman frequencies of BP(S_0) in BP/H_nZSM-$5^{\bullet-\bullet+}$ were observed in the spectra recorded at 370 and 1064 nm (Figure 1 c). All the Raman features were found to be analogous in terms of wavenumbers and relative intensities to those of BP/H_nZSM-5 obtained by sorption in H_3ZSM-5 dehydrated under argon for which spontaneous ionization does not occur (Figure 1 b). It should be noted that the relative intensities differ markedly for BP in a nonpolar environment (silicalite-1; Figure 1 a). These findings indicate low local symmetry and an intense electrostatic field at the sorption site. After the disappearance of the characteristic electronic absorption bands of $BP^{\bullet+}$ at 370 and 650 nm, the

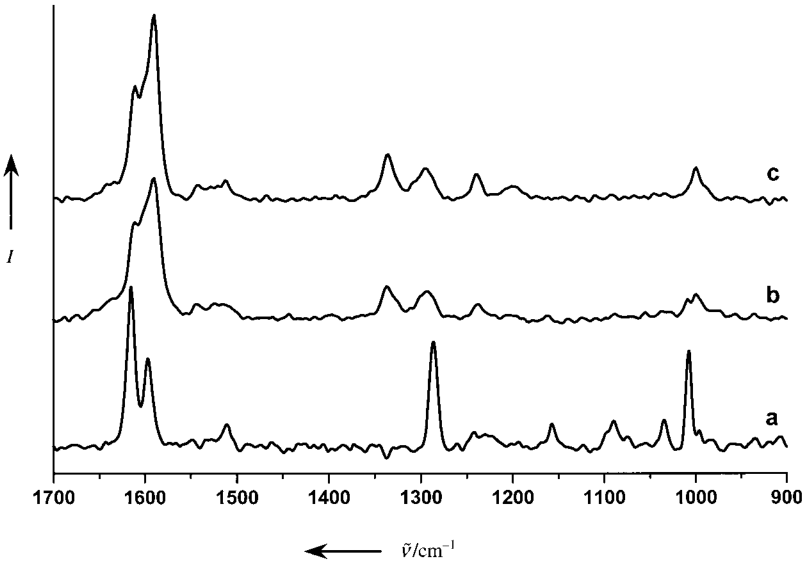

Figure 1. FT-Raman spectra (wavelength 1064 nm) of biphenyl (BP) occluded in silicalite-1,$(SiO_2)_{192}$ (a), in H_3ZSM-5, $H_3(AlO_2)_3(SiO_2)_{189}$, dehydrated under argon (b), and in H_3ZSM-$5^{\bullet-\bullet+}$ after the disappearance of the radical cation $BP^{\bullet+}$, $H_3(AlO_2)_3(SiO_2)_{189}$, activated under O_2 and evacuated under vacuum (c). I = Raman intensity in arbitrary units.

diffuse reflectance (DR)UV-Vis absorption spectrum exhibits an intense broad absorption around 500 nm in addition to the characteristic band at 250 nm displayed by occluded BP. No evidence of $BP^{\bullet -}$ (400, 610 nm) was observed. The persistent absorption at 500 nm was correlated with the appearance of a featureless continuous-wave (CW)-EPR signal (Figure 2); the seven-line spectrum of $BP^{\bullet +}$[7, 10, 14] dissappeared and was replaced by a broad signal around $g = 2$.[10]

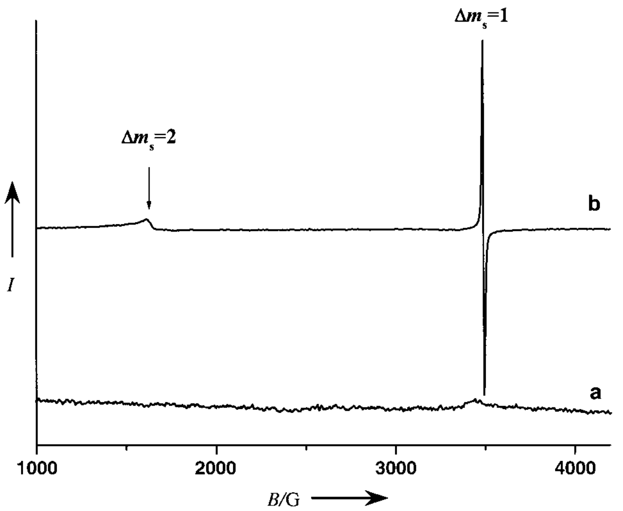

Figure 2. CW X-band EPR spectra of the H_3ZSM-5 zeolite calcined at 800 K under O_2 and evacuated under vacuum (a), and biphenyl occluded in the $H_3ZSM\text{-}5^{\bullet - \bullet +}$ zeolite (one BP molecule per unit cell) six months after the sorption (b). The spectra were recorded at 100 K with a modulation amplitude of 1 G and at a microwave power of 10 mW.

The strong signal around $g = 2$, which is typical of BP/$H_nZSM\text{-}5^{\bullet - \bullet +}$, remains broad even at low temperature (Figure 2b). The EPR signal and electronic absorption were found to be persistent over at least one year. The densities of unpaired electrons were estimated by double integrals of the EPR signals to be 0.3, 1.0, and 7.0×10^{-2} per unit cell for BP/$H_nZSM\text{-}5^{\bullet - \bullet +}$ with $n = 1$, 2, and 3, respectively, after several months under our experimental conditions. The electron-hole yield in BP/$H_nZSM\text{-}5^{\bullet - \bullet +}$ increases with Al content and temperature of calcination under O_2. With a spin density of less than 7.0×10^{-2} per unit cell and an assumed random distribution, the unpaired electrons would be separated on average by more than 70 Å and no interaction would occur between the unpaired electrons. Applying CW-EPR as a function of temperature we were able to characterize the magnetic exchange coupling between unpaired electrons of BP/$H_nZSM\text{-}5^{\bullet - \bullet +}$. A weak signal at a g value of about 4.22 is clearly visible and can be attributed to the forbidden transition $\Delta m_s = 2$ in a spin triplet $S = 1$, resulting from an electronic spin-coupling interaction ($S = 1/2$). The Boltzmann fitting of $g = 2.0036$ to the double integral signal of several spectra recorded from 10 to 300 K yields a value for the magnetic coupling constant of approximately 0.2 cm^{-1}. This results from population of the triplet state at low temperature. Thus, there is no doubt that the occluded electron-hole pair acquires a ferromagnetic ground state. The coupling constant estimates were not found to depend on the spin density, and the ferromagnetic exchange value is representative of individual electron-hole pairs in BP/$H_nZSM\text{-}5^{\bullet - \bullet +}$.

No hyperfine interaction was detected in the broad persistent signal of the CW-EPR spectra even at low temperature. To determine the structural surroundings of the unpaired electrons within BP/$H_3ZSM\text{-}5^{\bullet - \bullet +}$ we performed pulsed EPR experiments. Electron spin echo envelope modulation (ESEEM) spectroscopy measures the energy splittings of nuclei whose spins interact with the spin of unpaired electrons. These energy splittings were used to determine the nature of the electron nucleus environments. Significantly higher resolution was achieved in a two-dimensional (2D) four-pulse, hyperfine sublevel correlation (HYSCORE) spectroscopy experiment.[15–17]

The results of such an experiment are displayed in Figure 3a, which shows five ridges centered at a proton nuclear Larmor frequency of 14.5 MHz. We can directly measure an anisotropic hyperfine constant of 9 MHz. An additional peak centered at 2.9 MHz corresponds to a ^{29}Si free nuclear Larmor frequency resulting from a ^{29}Si nucleus coupling with an

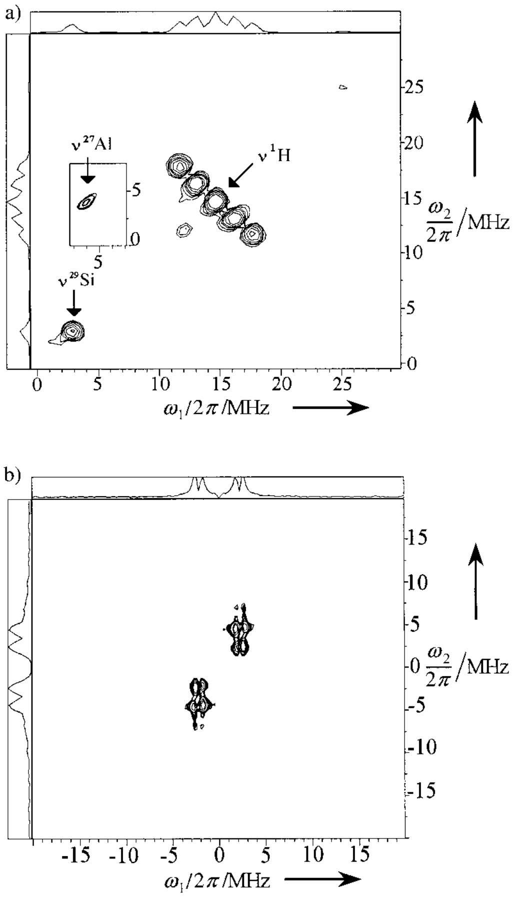

Figure 3. a) HYSCORE spectrum of an $[H_{10}]$biphenyl molecule occluded in the $H_3ZSM\text{-}5^{\bullet - \bullet +}$ zeolite (1 BP/H_3ZSM-5) six months after the sorption. The spectrum was obtained at the maximum of the EPR signal at 300 K at $\tau = 256$ ns and at 4.2 K (framed) at $\tau = 200$ ns. Pulse lengths of 12 ns for $\pi/2$ pulses and 24 ns for the π pulse were used, and a four-step phase cycling ($\pi/2$-τ-$\pi/2$-t_1-π-t_2-$\pi/2$-τ-echo) was applied to suppress unwanted echo. b) Two-dimensional, three-pulse ESEEM spectrum of $[D_{10}]$biphenyl occluded in the $H_3ZSM\text{-}5^{\bullet - \bullet +}$ zeolite (1 BP/H_3ZSM-5) six months after the sorption. Pulse lengths of 12 ns were set for the $\pi/2$ pulses.

electron. When the experiments were carried out at 4.2 K another peak centered at 3.8 MHz can be assigned to the free Larmor nuclear frequency of ^{27}Al nuclei (see frame in Figure 3a). No coupling of a ^{13}C nucleus with an electron was detected. To establish the origin of the proton modulation, we performed the experiment with fully deuterated $[D_{10}]$BP. The substitution of the ^{1}H by the ^{2}H isotope in BP dramatically affects the two-dimensional, three-pulse ESEEM spectrum (Figure 3b). These findings indicate that the ^{1}H or ^{2}H isotope of BP are the main contributors to these lines. The proton modulation has effectively completely disappeared but a strong deuterium pattern is observed. The corresponding HYSCORE spectra (not shown) yield an anisotropic coupling constant of 1.6 MHz. In contrast, the substitution of ^{1}H by ^{2}H in the bridging OH group of the H_3ZSM-5 zeolite, and subsequent $[H_{10}]$BP sorption does not affect the CW EPR spectrum. However, the two-pulse ESEEM spectrum reveals a strong ^{1}H pattern modulation with an overlapped weak ^{2}H pattern modulation. Removing proton modulation by high pass filtering gives, after Fourier transformation, a single signal centered at 2.2 MHz, which is assigned to a ^{2}H nuclear Larmor frequency. ESEEM spectroscopy results strongly suggest that the unpaired electrons are located near Al and Si atoms of the zeolite framework and in the vicinity of H atoms of occluded BP. There is no experimental evidence to assign the trapped electron and the positive hole.

The experimental investigations on the presented system provide a reasonable picture of the electron-hole pairs that are stabilized indefinitely in the self-assembled array of BP/H_nZSM-$5^{\bullet-\bullet+}$. The biphenyl molecule lies in the ground state in the channel of the zeolite in close proximity to the Brønsted acid site. The electron and positive hole appear separated by the occluded biphenyl molecule and efficiently trapped in the neighboring side pockets of the channel. The magnitude of the ferromagnetic exchange interaction appears to be related to the electronic structure of the path between the two paramagnetic centers.

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