of interactions between paramagnetic molecules can be given. The X-band EPR spectrum of **1** in a frozen ethanol glass is available in the supplementary material. The 7 K spectrum consists of a typical axial pattern ($g_{\parallel} = 3.56$, $g_{\perp} = 1.74$, and $\Delta g = 1.82$) with no $g \simeq 2$ feature. As the temperature is increased, this axial signal broadens and becomes unobservable above 77 K with no appearance of a $g \simeq 2$ signal. Consequently, this indicates that the $g \simeq 2.16$ signal seen for the polycrystalline sample is likely the result of intermolecular interactions in the magnetically concentrated conditions of a crystalline lattice. It is unlikely that the $g \simeq 2.16$ signal represents cations which are electronically delocalized for several reasons. First, the IR spectrum of electronically delocalized species show a single C–H bending vibration midway between that of an Fe^{II} and Fe^{III} metallocenes. Two C–H bending bands, one characteristic of Fe^{II} and the other Fe^{III}, are seen in the IR spectrum of **1**.[10] Second, an electronically delocalized species still shows some residual *g*-tensor anisotropy.[24]

X-band EPR spectra collected on different microcrystalline samples of **1** serve to illustrate further the extreme "environmental" sensitivity that this mixed-valence complex exhibits. The spectrum at 7 K of four different polycrystalline samples together with that for the ethanol glass sample are shown in Figure 9. All of these spectra are the superposition of a number of signals. The exact position of the $g_{\parallel}$ features for the various polycrystalline samples varies appreciably from one sample to another. All of these polycrystalline samples exhibit only the $g \simeq 2$ signal when the temperature is increased.

Concluding Comments. The polymorphism discovered for 1′,1‴-dibenzylbiferrocenium triiodide definitively shows that the immediate environment of the mixed-valence cation plays an important role in determining the rate of intramolecular electron transfer. In the $P\bar{1}$ polymorph of **1** the electron-transfer rate is faster than 10^9 s^{-1} above ~25 K, while in the $P2_1/n$ polymorph the rate is slower than 10^6 s^{-1} for all temperatures. The only differences between the cations in these salts are attributable to their environment. The most extreme environmental control of the rate of intramolecular electron transfer is seen by mildly grinding the $P\bar{1}$ polymorph of complex **1**. The original sample is valence detrapped down to ~25 K. Grinding leads to a portion of the polycrystalline solid to remain trapped up to 310 K. This is a surprising result in view of the fact that the powder X-ray diffraction data show that there is no change in space group upon grinding. The environment can turn on or off the electron transfer.

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Supplementary Material Available: Complete tables of positional parameters, bond lengths and angles, and thermal parameters for the $P\bar{1}$ form of complex **1** at 298 and 135 K, table of Mössbauer parameters for a ground sample of the $P\bar{1}$ polymorph of complex **1**, tables of positional parameters, thermal parameters, and bond lengths and angles for the $P2_1/n$ polymorph of complex **1** at 296 K, and figures showing powder X-ray patterns, temperature dependence of the X-band EPR spectrum of the frozen ethanol glass of complex **1**, and a packing diagram of the $P2_1/n$ polymorph of complex **1** (17 pages); tables of observed and calculated structure factors for the $P\bar{1}$ form of complex **1** at 298 and 135 K and the $P2_1/n$ polymorph of complex **1** at 296 K (88 pages). Ordering information is given on any current masthead page.

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Selective Two-Component Self-Diffusion Measurement of Adsorbed Molecules by Pulsed Field Gradient Fourier Transform NMR

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Abstract: The two-component self-diffusion of C_2H_4 and C_2H_6 adsorbed in NaX zeolite crystals has been measured by ^1H pulsed field gradient (PFG) Fourier transform NMR. The results so obtained are compared with single-component self-diffusion measurements and with values for the intracrystalline mean residence times, determined by means of NMR tracer desorption experiments.

Application of the PFG NMR method[1] to diffusion studies in zeolitic adsorbate–adsorbent systems[2,3] has substantially contributed to a deeper understanding of molecular migration in the interior of zeolite crystallites.[4,5] This development was in particular stimulated by the ability of PFG NMR to monitor directly the intracrystalline molecular displacements. As a substantial advantage in comparison to the traditional way of studying intracrystalline diffusion by following the rate of molecular uptake, this peculiarity of PFG NMR implies the possibility of determining the diffusivities of individual components within a multicomponent system. Since during their technical application zeolites will be generally used under the conditions of multicomponent adsorption,[5] the significance of selective diffusion studies is obvious.

The traditional way of performing such experiments is to use perdeuterated compounds or compounds without any hydrogen so that only one of the various compounds yields the ^1H NMR signal[2] from which the diffusivity may be easily determined. Unfortunately, this way of selective diffusion measurement necessitates additional experimental preparation, since for the study of a system containing *n* components at least *n* various NMR samples must be prepared, each of them with a different compound in the hydrogen form.

A more straightforward possibility of selective self-diffusion measurements is provided by Fourier transform NMR. In this method the total NMR signal is split up in separate signals of

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the constituents if these exhibit different NMR spectra (chemical shifts).[6] This procedure has been successfully applied to multicomponent liquids[7,8] where it was possible to measure the self-diffusion coefficients of up to eight different components[8] since in this case, owing to the high molecular mobility, the line widths were small enough to allow a resolution of the observed NMR spectra into the spectra of the individual components.

As a consequence of the reduced molecular mobility, similar experiments have not yet been performed with adsorbate–adsorbent systems. Most promising prospects for such experiments are evidently provided for systems of sufficiently high mobility and with large differences in the chemical shifts of the individual components. Following previous single-component self-diffusion studies,[9,10] we have considered therefore the two-component self-diffusion of the short-chain-length molecules ethane and ethene in the large-pore zeolite NaX.

Theoretical Section

PFG NMR is based on the application of a radio-frequency pulse sequence ($\pi/2-\tau-\pi$) for generating a transient NMR signal (the spin–echo) at time τ after the second radio-frequency pulse (the π pulse). In addition to this pulse program, over two short intervals of duration δ the constant magnetic field is superimposed by an inhomogeneous field with a large field gradient g. Under the influence of these "field gradient pulses" the spin–echo intensity is reduced by a factor[1,2,7,8,11]

$$\Psi(\delta g,\Delta) = \exp\{-\gamma^2\delta^2g^2\langle r^2(\Delta)\rangle/6\} \qquad (1)$$

with Δ denoting the separation between the two field gradient pulses. γ stands for the gyromagnetic ratio. $\langle r^2(\Delta)\rangle$ denotes the mean square displacement of the molecules under study during the "observation time" Δ, i.e. the time interval between the two gradient pulses. Equation 1 implies that the probability distribution (the "propagator") of the diffusing molecules is given by a Gaussian function and that the width δ of the gradient pulses is sufficiently small in comparison to the observation time Δ ($\delta/3 \ll \Delta$).

In homogeneous systems, according to Einstein's relation

$$\langle r^2(\Delta)\rangle = 6D\Delta \qquad (2)$$

the self-diffusion coefficient D follows easily from the slope of the plot of the mean square displacement over the observation time Δ. In conventional PFG NMR, the total signal attenuation of multicomponent systems will result as a superposition of various terms of the type of eq 1 with mean square displacements corresponding to those of the individual components and with relative intensities determined by the contribution of the individual components to the spin–echo. In this way, a simultaneous determination of the diffusivities of different components is only possible for vastly different diffusivities.[12] Transformation of the spin–echo into the frequency domain, however, provides a straightforward possibility of separating the overall signal into its constituents, characterized by the differences in their chemical shift. We assume for simplicity that the mixture consists of only two constituents A and B and that the ^{1}H NMR spectra of both constituents is given by a single line with resonance frequencies ω_A and ω_B, respectively. Introducing the chemical shifts δ_{HA} and δ_{HB}, the necessary condition for a PFG Fourier transform experiment is that the separation

$$\omega_A - \omega_B = (\delta_{HA} - \delta_{HB})\gamma B_0 \qquad (3)$$

between the individual lines is larger than or at least of the order of the line widths $\Delta\omega$. Assuming that the inhomogeneity of the constant magnetic field can be neglected, the line widths are connected with the transverse nuclear magnetic relaxation time T_2:

$$\Delta\omega_{A(B)} = 2/T_{2A(B)} \qquad (4)$$

Zeolitic adsorbate–adsorbent systems may be considered to be quasihomogeneous as long as the molecular mean square displacements during the observation time Δ are much less than the mean crystallite diameter. In this case the majority of the molecules will not interfere with the crystallite surface and may be considered, as if being within a homogeneous system of infinite dimensions. As soon, however, as the molecular mean displacements are not much less than the mean crystallite dimensions, two peculiarities must be considered in comparison to the behavior in homogeneous systems:

(i) Since now during the observation time a perceptible number of molecules may be able to leave their crystallites, echo attenuation is possibly a superposition of two exponentials of the type of eq 1, corresponding respectively to the molecules remaining in the interior of the individual crystallites (relative intensity $1 - \Gamma(\Delta)$) and those leaving their crystallites (relative intensity $\Gamma(\Delta)$). Since, in general, the mean square displacement of the molecules leaving their crystallites is much larger than the mean square displacement of those which remain in the crystallites, both contributions may in general be easily separated from each other. In this way one may directly determine the relative amount of molecules exchanging between the individual crystallites and the surrounding gas phase. This is just the same information as provided by conventional tracer exchange experiments. The method has been called, therefore, the NMR tracer desorption technique[13] or, in view of the short observation times (milliseconds), fast tracer desorption.[5]

(ii) The mean square displacement of the molecules in the interior of the crystallites cannot increase infinitely. It is confined to a maximum value of the order of the mean square crystallite radius.[9] Hence as soon as the molecular displacements are not much less than the crystallite diameters, eq 2 is no longer valid and $\langle r^2\rangle$ increases less than proportional with increasing observation time.[11]

Experimental Section

We have employed a specimen of zeolite NaX with a mean crystallite diameter of 60 μm, provided by Zhdanov and Feoktistova.[14] As previously described,[15] PFG NMR measurements have been carried out with the loaded zeolites contained in sealed glass tubes with an outer diameter of 10 mm and a filling height of about 20 mm. For sample preparation, the zeolite material has been spread as a thin layer with a depth of less than 3 mm and heated under continuous evacuation with a heating rate of 10 K/h until a final temperature of 673 K and a final pressure of less than 0.1 Pa were reached. The two adsorbate components, ethane and ethene, have been consecutively introduced into the thus activated sample by freezing in a bath of liquid nitrogen from a well-defined volume at room temperature. The achieved loading (1.5 molecules of ethane and 1 molecule of ethene per supercage) was checked by comparing the intensities of the two ^{1}H NMR lines. The uncertainty in the loading is ±0.1 molecules per supercage.

The ^{1}H PFG NMR self-diffusion measurements have been carried out at 293 K by means of a home-built spectrometer (UDRIS) at a resonance frequency of 90 MHz corresponding to an intensity $B = 2.1$ T of the constant magnetic field. The intensity g of field gradient pulses was 2.8 T/m. The pulse widths δ and observation times Δ were varied between 0.1 and 0.6 ms, and 2 and 15 ms, respectively. The rise and fall time of the gradient pulses (time interval between 90% and 10% of full intensity) was 50 μs,[11] so that even for the shortest observation times there was no interference between the gradient pulses and the echo.

It is common practice in the conventional PFG NMR to apply a constant magnetic field gradient in addition to the pulsed ones in order to compensate for possible mismatches between the two field gradient pulses.[8,11] In Fourier transform NMR, however, this procedure is not applicable: The field inhomogeneity brought about by such a constant gradient would lead to a significant broadening of the NMR lines, so that

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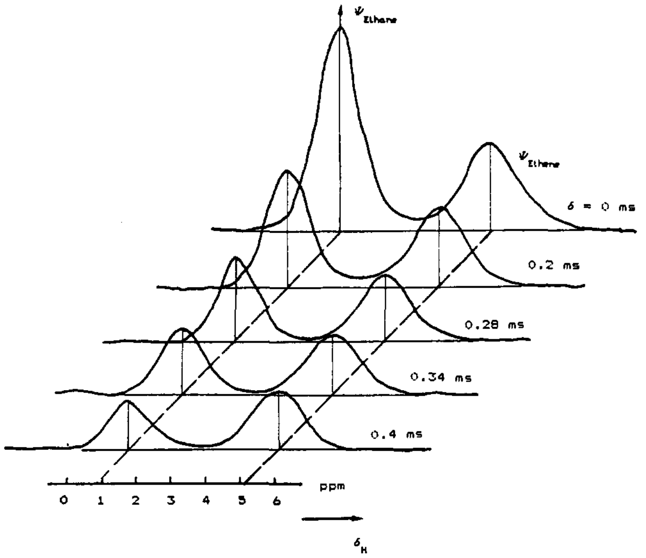

Figure 1. ^1H PFG Fourier transform NMR spectra of an ethane–ethene mixture (1.5 molecules of ethane and 1 molecule of ethene per supercage) adsorbed on zeolite NaX at 293 K for increasing values of the width δ of the field gradient pulses. The pulse separation (Δ) and the intensity (g) are 4 ms and 2.8 T m^{-1}, respectively. The chemical shifts δ_H refer to TMS.

their separation would become impossible. Differences in the "area" δg of the two field gradient pulses had to be minimized, therefore, by varying the width of the second field gradient pulse until the intensity of the spin–echo has become maximum. It has been checked by applying a sample with a sufficiently low diffusivity that in this case in fact complete refocusation of the NMR signal was achieved. The NMR spin–echo was accumulated up to 900 times, followed by Fourier transformation of the second half of the echo. The positions of the two lines (δ_H = 0.75 and 5.15 ppm; all data with respect to TMS) for ethane and ethene were in satisfactory agreement with literature data for the neat components (0.88,[16] 5.86 ppm[17]). Since the line widths were (1.3 ± 0.6) ppm and (1.7 ± 0.6) ppm, respectively, the line separation turned out to be large enough to allow a separate analysis of the attenuation of either of these lines under the influence of the field gradient pulses. The absolute values of the mean square displacements were obtained by comparison with the PFG NMR spin–echo decay of a sample with known diffusivity (neat water, 2.04×10^{-9} m^2 s^{-1} at 293 K[18]).

Results

As an example, Figure 1 shows ^1H PFG Fourier transform NMR spectra dependent on the applied field gradient width δ for an observation time Δ of 4 ms. Fitting eq 1 to the decay of the intensity of either of these lines yields mean square displacements of (105 ± 13) and (30 ± 4) μm^2 for ethane and ethene, respectively. Figure 2 shows the complete dependence of the mean square displacements on the observation time Δ. In those cases where during the observation time a perceptible number of molecules did escape from the intracrystalline space, the intracrystalline mean square displacements were determined from the second, slowly decaying part of the ln Ψ vs δ^2 representation. Due to the increasing influence of transverse nuclear magnetic relaxation the uncertainty of the experimental data as indicated by the error bars became larger with increasing values of the observation time Δ. Thus during the considered range of Δ any deviation from linearity which should occur if the root mean square displacements are not much less than the diameter of the crystallites remained within the limits of uncertainty of the measurements. This is in agreement with theoretical estimates[11] where for mean square displacements of the order of 20% of the limiting value for infinite observation times a deviation of no more than 10% in comparison to the case of unrestricted diffusion may be expected. A weighted least-squares fit of eq 2 to the experimental values of Figure 2 yielded the self-diffusion coefficients (4.6 ± 0.9) × 10^{-9} m^2 s^{-1} for ethane and (1.25 ± 0.25) × 10^{-9} m^2 s^{-1} for ethene.

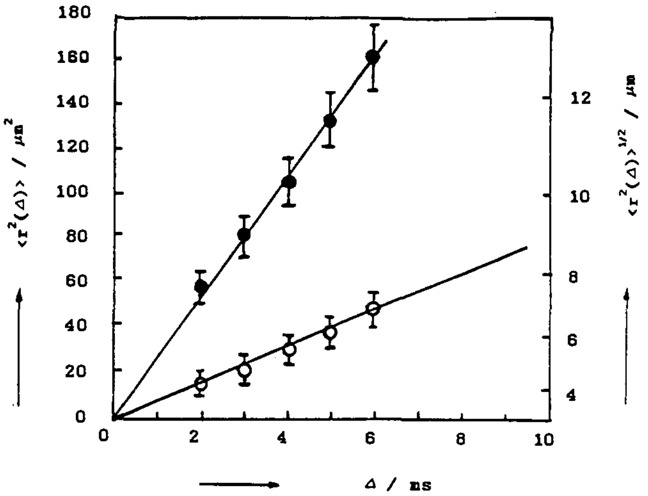

Figure 2. Mean square displacements of ethane (●) and ethene (○) in a 3:2 mixture, adsorbed on a NaX zeolite with a loading of (total) 2.5 molecules per cavity. The mean diameter of the crystallites is 60 μm and the measuring temperature is 293 K.

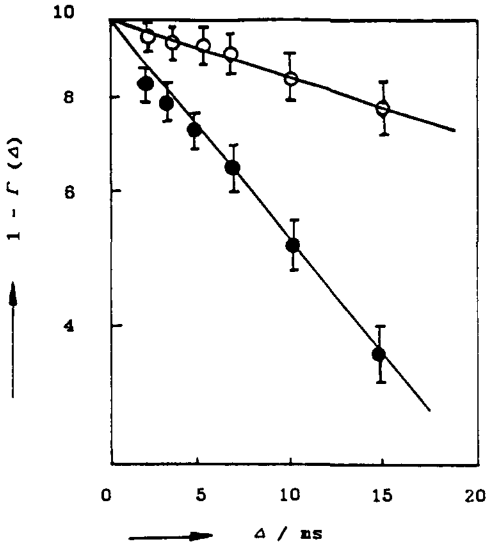

Figure 3. NMR tracer desorption curves for ethane (●) and ethene (○) adsorbed on a NaX zeolite (cf. Figure 2) at 293 K. 1 – Γ(Δ) represents the relative number of molecules which during the observation time Δ have not yet left their crystallites.

Figure 3 shows the dependence of the quantity 1 – Γ(Δ), i.e. the relative number of molecules which during Δ do not leave their crystallites, relative to the observation time Δ. For a quantitative discussion it is convenient to introduce the intracrystalline mean lifetime by the relation[4,13]

$$\tau_{\text{intra}} = \int_0^\infty (1 - \Gamma(\Delta))\, d\Delta \qquad (5)$$

Approximating the experimental data by a simple exponential dependence

$$\Gamma(\Delta) = 1 - \exp(-\Delta/\tau_{\text{intra}}) \qquad (6)$$

the value for the intracrystalline residence times τ_{intra} are found to be (15 ± 4) and (60 ± 15) ms, respectively.

Discussion

In previous single-component PFG NMR measurements of ethane[9,10] and ethene[10] adsorbed on zeolite NaX with the same (total) sorbate concentration of about 2.5 molecules per supercage,

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self-diffusivities of 1.1×10^{-8} and 1.25×10^{-9} $m^2\ s^{-1}$ were obtained. Hence it turns out that in the mixture the difference in the mobility of the two components is much less than for single-component adsorption. Such behavior is well-known from the investigation of multicomponent liquids[7,8] and may be understood as a consequence of the interaction between the different diffusants. It is interesting to note that in comparison to single-component adsorption the diffusivity of ethene remains essentially unchanged, while the ethane diffusivity is distinctly reduced. One has to conclude, therefore, that encounters between unlike molecules within the intracrystalline pore system predominantly reduce the mobility of the (more mobile) ethane molecules rather than enhance the mobility of the (more strongly bounded) ethene molecules.

Under the assumption that no additional transport resistance ("surface barriers"[2,19]) exists at the external surface of the zeolite crystallites, the mean intracrystalline residence time may be easily calculated from the size of the crystallites and the coefficient of intracrystalline self-diffusion.[4] For crystallites of spherical shape (which generally is a sufficiently good approximation) one has[2,4,13]

$$\tau^{D}_{\mathrm{intra}} = \langle R^2 \rangle / 15 D_{\mathrm{intra}} \qquad (7)$$

where $\langle R^2 \rangle$ denotes the mean square crystallite radius. Inserting the intracrystalline diffusivities determined by PFG Fourier transform NMR for the two components into eq 7 yields values of 13.5 and 48 ms, respectively. These data are in satisfactory agreement with the values for the real intracrystalline mean lifetimes τ_{intra} following from the NMR tracer desorption curves represented in Figure 3. One has to conclude, therefore, that for either of the adsorbed components the crystallite surface does not exert any significant transport resistance. This result is in agreement with previous single-component PFG NMR investigations[13,15] where, in contrast to the small pore A type zeolites, the more open NaX structure was found to show no tendency to forming surface barriers.

Conclusion

PFG Fourier transform NMR has been successfully applied to measure selectively the self-diffusion coefficients in a two-component mixture adsorbed on microporous adsorbents.

In an ethane–ethene mixture adsorbed on zeolite NaX the diffusivity of the ethene molecules is by a factor of 3 to 4 smaller than the mobility of ethane. This result may be understood as a consequence of the specific interaction of the unsaturated hydrocarbons with the sodium cations. As a consequence of the mutual interaction between the two components this difference is distinctly smaller than that for single-component adsorption. The values for the mean intracrystalline residence times of both components estimated from these intracrystalline diffusivities are in satisfactory agreement with the results directly determined by NMR tracer desorption studies. This experimental finding provides an independent check of the correctness of the measured diffusivities, and in agreement with previous studies, a significant influence of additional transport resistances on the outer surface of the crystallites (surface barriers) may be excluded.

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Resonance Raman Studies of Oxycytochrome P450cam: Effect of Substrate Structure on ν(O–O) and ν(Fe–O_2)

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Abstract: Resonance Raman spectra of dioxygen adducts of cytochrome P450cam, in the presence of various substrates, and their biomimetic analogues are reported. The oxidation marker band, ν_4, of oxycytochrome P450cam is observed at 1374 cm^{-1}, which is lower than that of oxyhemeproteins possessing histidyl as a proximal ligand, reflecting the presence of a strong electron-releasing thiolate axial ligand. Both the ν(O–O) and ν(Fe–O_2) modes are simultaneously observed and identified (by using $^{16}O_2/^{18}O_2$ isotopic substitution technique) at 1140 cm^{-1} and 541 cm^{-1}, respectively for camphor-bound oxygenated cytochrome P450cam. When camphor is replaced with adamantanone, two lines at 1139 cm^{-1} and 1147 cm^{-1} are observed for the ν(O–O) mode, while no significant change in heme core structure is discerned. The substantially lowered frequencies of the ν(O–O) and ν(Fe–O_2) and their sensitivity to the variation of the substrate structure provide a structural basis for cleavage of the bound dioxygen to generate a regio- and stereospecific hydroxylation agent.

Introduction

Cytochrome P450 includes a number of b-type heme proteins that have a characteristic electronic absorption band at 450 nm when combined with carbon monoxide in the reduced state.[1] They occur in many types of mammalian tissue, plants, and microorganisms and catalyze the incorporation of one atom of molecular oxygen into a vast variety of hydrophobic substances.[2] Because of their novel catalytic properties in the activation of dioxygen, they have received considerable attention in the past.[3] Among various cytochromes P450 that have been isolated, the water-soluble, three-component cytochrome P450 monoxygenase system, induced by camphor and isolated from the bacterium *Pseudomonas putida*, has been the most extensively characterized,[4] owing to its relative ease of handling. The recent X-ray crystallographic

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