

have large  $\delta_{22}$  and  $\delta_{33}$  components but negligible  $\delta_{11}$  component. The large steric effect that is observed for the ipso position with methoxyl and hydroxyl substitution then probably accounts for deviations of the substituent bond from the radial axis. If this factor is absent from the regression analysis, then an increase in the  $\delta_{11}$  component was found and a lower correlation coefficient. Additional steric factors may account for the observed large  $\delta_{11}$  ipso additivity factor with carboxyl and carbonyl substitution, but these were not considered because of the limited amount of data for these positions.

For carbon atoms ortho or para to an oxygen substitution site, the largest increments were observed on  $\delta_{11}$  and  $\delta_{22}$ . This can be explained by release of electrons from the oxygen atom to the  $\pi$ -orbitals of the ring. Additional electron density expands the carbon  $p_z$  orbitals, decreasing the  $\langle r^{-3} \rangle$  factor and, therefore, weakening the paramagnetic contribution along the  $x$  and  $y$  axes. A similar effect has been reported by Strub et al.<sup>21</sup> for aromatic rings with five, six, or seven carbon atoms.

Substitution had little effect on the chemical shifts for the meta carbons, and this is consistent with charge-density alternation around the ring.

### Conclusions

We have determined the principal values of the CST for aromatic carbons for a range of methoxyl- and hydroxyl-substituted benzene derivatives. With this large data set incorporated into a simple linear additivity model, the changes in the principal values of the CST with substitution can be predicted within a few parts per million.

Such uncertainties are small enough for the predicted CST principal values to be useful in quantitative CP/MAS NMR, through generation of correction factors to be applied to measurements of the center-band signal strength.

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## Intracrystalline Mass Transfer in Zeolites Monitored by Microscopic and Macroscopic Techniques

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**Abstract:** Conventional  $^1\text{H}$  NMR signal intensity measurements have been used to monitor macroscopically the kinetics of molecular exchange of deuterium-labeled molecules between the intracrystalline space of zeolite crystallites and the surrounding atmosphere. After reaching equilibrium, a pulsed-field-gradient experiment was performed within the same sample tube so that it became possible for the first time to compare results for the intracrystalline migration of adsorbed molecules derived from macroscopic (intensity) and microscopic (pulsed-field-gradient) measurements on identical samples. For benzene adsorbed on zeolite Na-X the intracrystalline diffusivities resulting from these two measuring techniques are found to be in satisfactory agreement. This result proves that molecular exchange between benzene adsorbed in the intracrystalline space of Na-X and the surrounding atmosphere is essentially controlled by intracrystalline mass transfer.

The advent of synthetic zeolites<sup>1</sup> has initiated a remarkable development in numerous branches of modern chemical technology.<sup>2,3</sup> It is basically the large, well-defined and modifiable intracrystalline pore volume of the zeolites that leads to their excellent properties as catalysts and molecular sieves. While, due to the combined application of X-ray scattering techniques,<sup>4,5</sup> high-resolution electron microscopy,<sup>6</sup> and magic angle spinning NMR,<sup>7-9</sup> a large variety of zeolite crystal structures are fairly

well-known, for more than one decade the rate of mass transfer within the intracrystalline pore system has been the topic of controversial discussion.<sup>10-17</sup> This controversy has been brought about by the exciting result of the first NMR pulsed-field-gradient experiments<sup>10,18</sup> that in several cases the intracrystalline molecular mobilities in zeolites are by up to 5 orders of magnitude larger than previously determined on the basis of molecular uptake measurements.<sup>19,20</sup> A critical reconsideration of the uptake technique led to the conclusion that in several cases molecular uptake was limited by processes whose time constants previously

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have been assumed to be negligibly small in comparison with intracrystalline diffusion.<sup>19-22</sup> However, even today there is still a remarkable divergency in the experimental results for intracrystalline molecular diffusion in zeolites. While in several cases uptake measurements are found to lead to results coinciding with the NMR technique,<sup>10,14,22-25</sup> in other experimental studies remaining differences of up to 2 orders of magnitude have been observed.<sup>13,15,17</sup>

On comparing the results of NMR pulsed field gradient and of the uptake measurements, one must have in mind that these two methods are based on observations on completely different scales of space and time. While in NMR pulsed-field-gradient experiments the distribution of molecular displacements are monitored with mean spatial distribution widths of the order of micrometers, i.e., essentially within the individual zeolite crystallites,<sup>18</sup> uptake measurements are following the molecular exchange between the zeolite bed and the surrounding atmosphere in the adsorption vessel.<sup>19-21</sup> Depending on the experimental conditions, by the latter technique, in principle, two different mass-transfer coefficients may be obtained:<sup>18-21</sup> (i) the coefficient of intracrystalline diffusion for measurements under nonequilibrium conditions, i.e., for uptake measurements induced by pressure variation in the surrounding atmosphere, or (ii) the coefficient of intracrystalline self-diffusion for measurements under macroscopic equilibrium. In the latter case, molecular exchange between the adsorbed and gaseous phases may be observed by replacing the molecules in either the adsorbed or gaseous states by isotope-labeled molecules and then by following the uptake by the other phase. It is this coefficient of intracrystalline self-diffusion that is also determined in the NMR pulsed-field-gradient experiments. Both techniques should yield, therefore, identical measuring quantities, provided that the molecular exchange in the tracer uptake measurements is in fact controlled by intracrystalline mass transfer.

As yet, all comparative NMR and uptake measurements have been carried out in different experimental setups. Since the transport properties of zeolitic adsorbate-adsorbent systems may in fact significantly depend on the way a sample is prepared and activated (as characterized, e.g., by bed configuration and the time programs of temperature and pressure,<sup>26-28</sup> as well as on the possible presence of residual molecules of different species (such as, e.g., water<sup>29</sup>), apparent differences<sup>30</sup> might, in principle, be referred to the fact that it is essentially impossible to have completely identical zeolite specimens in different experimental setups. The performance of tracer exchange and NMR pulsed-field-gradient measurements on identical samples has therefore become a key experiment for elucidating the correlation between macroscopic (uptake) and microscopic (NMR pulsed-field-gradient) diffusion measurements.

## Experimental Section

Simultaneous macroscopic and microscopic self-diffusion measurements may be carried out by taking advantage of the possibility of the <sup>1</sup>H NMR spectroscopy itself to monitor molecular exchange between the adsorbed and gaseous phases. For this purpose it is only necessary to

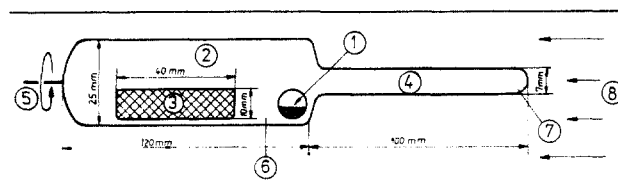


Figure 1. Experimental arrangement for the tracer-exchange and pulsed-field-gradient measurements: (1) Glass vial containing the zeolite with the perdeuterated adsorbate. The exchange process is started by crushing the glass vial by means of the container (3). Afterward, the zeolite crystallites are spread over the bottom of the vessel (position 6). (2) Adsorption vessel containing the adsorbate in the hydrogen form. (3) Cylindric glass container with holes at the faces containing granulated zeolite Na-X (rms radius of the crystallites ca. 1  $\mu\text{m}$ ) as a reservoir of the adsorbate in the hydrogen form. (4) Sample tube for both the NMR exchange and pulsed-field-gradient measurements, to be introduced into the rf coil of the NMR spectrometer. (5) Arrangement for keeping the adsorption vessel rotating at a speed of about 1  $\text{s}^{-1}$  in the intervals between the intensity measurements. (6) Position of the adsorbent crystallites during the exchange process. (7) Position of the adsorbent crystallites during the NMR measurements. (8) Temperature-controlling gas stream.

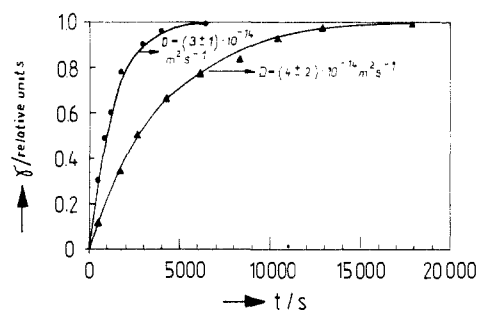


Figure 2. NMR tracer-exchange curves at 293 K for benzene on Na-X with an rms value for the radius of the crystallites of 25  $\mu\text{m}$  (●) and 50  $\mu\text{m}$  (▲), respectively. The loading of the zeolite corresponds to 4.8 molecules/cavity. The intracrystalline diffusivities were calculated on the basis of eq 1 and 2.

bring the zeolite crystallites containing the isotope-labeled (perdeuterated) adsorbate into contact with an atmosphere of the adsorbate in the unlabeled (hydrogen-containing) form. In this way, the relative amount of tracer uptake (and with it, respectively, of tracer exchange) is directly measured by the intensity of the <sup>1</sup>H NMR signal. In Figure 1 the experimental arrangement is shown and the procedure explained by which the comparative uptake and diffusion measurements have been carried out.<sup>31</sup> In our experiments, we have studied the transport properties of benzene in zeolite Na-X with values for the root-mean-square radius of the crystallites from 15 up to 60  $\mu\text{m}$  at a sorbate concentration of about 4.8 molecules/cavity, which is slightly less than the saturation capacity of about 5.1 molecules/cavity at 293 K.

In the tracer-uptake measurements, the intracrystalline self-diffusion coefficients have been calculated from the mean tracer exchange time  $\tau_{\text{intra}}$  via the equation<sup>18-20</sup>

$$D_{\text{intra}} = \langle R^2 \rangle / 15\tau_{\text{intra}} \quad (1)$$

where  $\langle R^2 \rangle$  denotes the mean-square radius of the zeolite crystallites.  $\tau_{\text{intra}}$  has been determined as the so-called first statistical moment of the tracer-exchange curve<sup>20</sup>

$$\tau_{\text{intra}} = \int_0^{\infty} (1 - \gamma(t)) dt \quad (2)$$

Here  $\gamma(t)$  denotes the relative amount of molecules exchanged at time  $t$ .

## Results and Discussion

Figure 2 presents typical experimental data for the tracer exchange obtained for two different crystallite sizes. Within the accuracy of the experimental procedure, the intracrystalline diffusivities obtained from these two curves via eq 1 and 2 are

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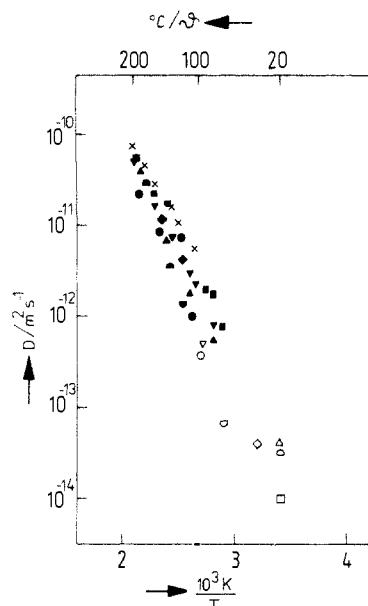


Figure 3. Comparison of the intracrystalline diffusivities obtained from tracer-uptake (open symbols) and NMR pulsed-field-gradient (full symbols) experiments. Identical symbols refer to measurements with identical samples. Previous results of NMR self-diffusion measurements ( $\times$ ) are shown for comparison.<sup>32</sup>

found to be in reasonable agreement, as to be required if mass transfer is in fact controlled by intracrystalline transport. The definite check, however, is only possible by the comparison with the coefficients of intracrystalline diffusion directly obtained by the NMR pulsed-field-gradient technique. These coefficients have been determined in the traditional way by monitoring the amplitude of the NMR signal (the "spin-echo") for increasing pulsed-field-gradient intensities and by comparing the obtained attenuation with that observed for a standard with known diffusivity under identical conditions.<sup>18</sup> Obviously, in contrast to the tracer-exchange experiment, pulsed-field-gradient measurements can be carried out several times with the same sample.

Figure 3 provides a comparison of the values for the intracrystalline diffusivities obtained from the "macroscopic" NMR tracer uptake and the "microscopic" NMR pulsed-field-gradient measurements. Due to the different space and time scales of the NMR and uptake measurements, for a given size of the zeolite crystallites, if at all, there is only a small region of diffusivities accessible by both techniques.<sup>19,20</sup> As a consequence of this fact, in the present study the temperature regions of measurement only touch rather than overlap each other. It turns out, however, that there is a completely steady transition between the results of both measuring techniques. In addition, at 373 K it was possible to carry out the tracer uptake and the NMR pulsed-field-gradient measurement at the same temperature. Within the experimental uncertainty of a factor of about 2, both results are in reasonable

agreement. Thus the macroscopic and microscopic measuring techniques are found to lead to the same results. In addition, due to this agreement one has to conclude that under the given experimental conditions molecular exchange between the adsorbed and gaseous phases is indeed controlled by intracrystalline mass transfer.

It should be noted that the data presented in Figure 3 are quite close to the self-diffusion coefficients estimated from nonequilibrium (uptake<sup>19</sup> and zero-length column chromatographic<sup>15,17</sup>) measurements by means of the so-called Darken relation

$$D = D_d d[\ln c(p)]/d(\ln p) \quad (3)$$

with  $c(p)$  and  $D_d$  denoting, respectively, the sorbate concentration at sorbate pressure  $p$  and the diffusion coefficient obtained in the nonequilibrium measurements. However, while the nonequilibrium measurements thus analyzed yield fairly constant values of  $D$  over the whole concentration range, the NMR measurements have shown that the self-diffusion coefficients increase over nearly 2 orders of magnitude with decreasing concentration.<sup>32</sup> As yet it is unclear how the different concentration dependences are to be attributed to the peculiarities of the different measuring procedures.

Figure 3 shows that by the combination of the NMR tracer-uptake measurements with the pulsed-field-gradient technique, in the temperature interval under consideration self-diffusivities ranging over 4 orders of magnitude are covered. The activation energy determined in this way is equal to  $(55 \pm 15)$  kJ/mol. The activation energies previously determined by both pulsed-field-gradient measurements ( $\approx 40$  kJ/mol<sup>32</sup>) and uptake experiments ( $\approx 30$  kJ/mol<sup>17,24</sup>) for temperatures between about 400 and 500 K are at or even beyond the lower limit of this interval. One must be aware of the fact, however, that (i) different zeolite samples may in fact lead to slightly differing diffusivities and that (ii) the mechanism of molecular migration may change with decreasing temperature. In both cases deviations in the (overall) activation energies as deduced from Figure 3 with the previously determined values are possible.

### Conclusion

By applying the NMR pulsed-field-gradient technique in combination with the new NMR tracer uptake method, it could be demonstrated that the translational mobility of benzene molecules in the interior of Na-X type zeolite crystallites is as large as one has to expect on the basis of the molecular exchange rates between the intracrystalline and intercrystalline phases. One has to conclude, therefore, that for the system under consideration there are no additional transport resistances reducing the rate of molecular exchange between the crystallites and the intercrystalline space, thus guaranteeing that the macroscopic and microscopic measurements may in fact lead to the same result.

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