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Predicting Gas Transport in Formed Zeolite Adsorbents from NMR Studies

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The self-diffusion of nitrogen, methane, and carbon monoxide within a 5A zeolitic adsorbent has been examined by using pulsed field gradient (PFG) NMR. In all cases, the diffusion process is well-described by a refined version of the long-range diffusion model (LRDM),[1] adapted here for use with pelletized adsorbents, which uses exclusively adsorbent porosity and isotherm data as inputs. Correlation of the experimental data with the LRDM yields tortuosity factors that are characteristic of the adsorbate and reflect the longer diffusive path a molecule must take due to the winding nature of the pore structure (see Figure 1).

The modified LRDM has been evaluated by[2] (1) correlating pure gas diffusion as a function of pressure, (2) predicting gas diffusion in multicomponent gas systems, and (3) predicting diffusion behavior when pressure, temperature, and surface excess are changed simultaneously. Here we report results for pure gas and ternary gas mixture diffusion within a 5A zeolite.

The (self-) diffusion coefficient of gases in microporous adsorbent materials is among the most important parameters describing mass transfer through adsorbent beds.[3] Mass transfer through a zeolitic material depends on both intra- and intercrystalline diffusion processes where the transport within zeolitic crystals, i.e., intracrystalline diffusion, is experimentally found to be several orders of magnitude slower than intercrystalline diffusion. Despite this result intercrystalline diffusion is generally the dominant resistance in gas separation processes since typical pellet diameters are 4 to 5 orders of magnitude larger than zeolitic crystals.[3]

In this work, we have applied ^{15}N, ^{1}H, and ^{13}C-PFG NMR to investigate the self-diffusion of nitrogen, methane, and carbon monoxide within pelletized 5A materials in the pressure range from 0.5 to 5 atm. The experimental setup and method have been previously described in detail.[4,5] The echo attenuation Ψ was measured with use of PFG NMR on a Bruker AMX 360 spectrometer. In the case of normal diffusion the echo attenuation obeys the relation $\Psi = \exp(-q^2 D\Delta)$ with $\langle r^2 \rangle = 6D\Delta$, where Δ is the diffusion time and q is the abbreviation for $q = \delta\gamma g$. Here, δ is the duration of the gradient pulse, g is the strength of the gradient pulses, and γ is the gyromagnetic ratio of the investigated nucleus (e.g., ^{1}H, ^{13}C, ^{15}N). D is the self-diffusion coefficient and $\langle r^2 \rangle$ the mean square displacement of the molecules.

The most applicable theory available to describe self-diffusion behavior in microporous particles was developed by Kärger et al.[1] and has been shown to *qualitatively* represent self-diffusion in microporous crystalline *powders* by assuming that the long-range self-diffusivity (D^{LR}) is governed predominantly by transport through intercrystalline space. Although developed in the early 1980s, this model has never been critically evaluated since the pore structure of a powder sample could not be fully characterized. Unlike powders, however, the pore structure of a pelletized material is easily characterized by mercury intrusion and helium pycnometry measurements. Our goals in this work, therefore, were to (i) extend Kärger's model to describe transport in *pelletized* zeolites and (ii) stringently test the revised model's performance.

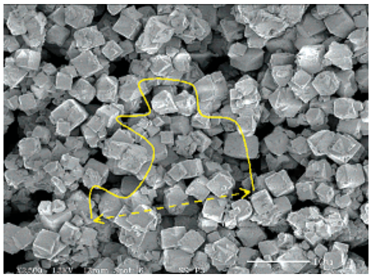

Figure 1. Micrograph picture of a 5A zeolite. The dashed line shows an idealized diffusion path described by the LRDM while the full line represents a more realistic diffusion path. The ratio of the theoretical and experimental diffusion coefficients yields a tortuosity factor that is characteristic of the adsorbent.

The value of $D_{\mathrm{i}}^{\mathrm{LR}}$ for a diffusant i within a pelletized sample can be approximated by the relationship $D_{\mathrm{i}}^{\mathrm{LR}} \cong p_{\mathrm{i}}^{\mathrm{inter}} D_{\mathrm{i}}^{\mathrm{inter}}$. The factor $p_{\mathrm{i}}^{\mathrm{inter}}$ represents simply the ratio of the number of molecules (of species i) in the macro-mesopore space to the total number of molecules of species i in the particle and $D_{\mathrm{i}}^{\mathrm{inter}}$ is their self-diffusivity. The value for $p_{\mathrm{i}}^{\mathrm{inter}}$ can be calculated directly from the adsorption isotherm as well as the characteristic dimensions of the particle from

$$\boldsymbol{p}_{\mathrm{i}}^{\mathrm{inter}} = \frac{c_{\mathrm{i}}\epsilon_{\mathrm{ma}}}{c_{\mathrm{i}}\epsilon_{\mathrm{ma}} + \rho_{\mathrm{p}} n_{\mathrm{i}}^{\mathrm{m}}} = \frac{1}{1 + [RT\rho_{\mathrm{p}} n_{\mathrm{i}}^{\mathrm{m}}/p_{\mathrm{i}}\epsilon_{\mathrm{ma}}]} \qquad (1)$$

Here c_{i} is the gas-phase concentration of component i (mol/cm^3 macro-mesopore), $n_{\mathrm{i}}^{\mathrm{m}}$ is the surface excess of species i (mol/g), ϵ_{ma} is the macro-mesopore porosity, ρ_{p} is the particle density, p_{i} is the partial pressure of component i, R is the gas constant, and T is the absolute temperature. Finally, the value of $D_{\mathrm{i}}^{\mathrm{inter}}$ can be estimated simply by using the kinetic theory of gases.[6]

To fully characterize a diffusive process, temperature, pressure, and surface excess must be clearly defined. Although the sample temperature within the NMR chamber is regulated, the pressure within an NMR sample and, consequently, the equilibrium loading on the adsorbent cannot be measured directly. The loading and the gas-phase pressure can be calculated, however, if an experimentally measured isotherm is available. Pure-component isotherm data are readily available and easily accessible, however multicomponent equilibria are generally not measured. To address this deficiency we have developed a gas-phase NMR method that enables equilibrium measurements to be performed directly on the samples which we are using for PFG NMR studies.[7] The reliability of the technique has been confirmed by comparison with nitrogen, methane, and carbon monoxide isotherms within a 5A adsorbent measured by standard volumetric techniques between the pressure range of 0.5 and 5 atm (Figure 2). In contrast to the gas-phase

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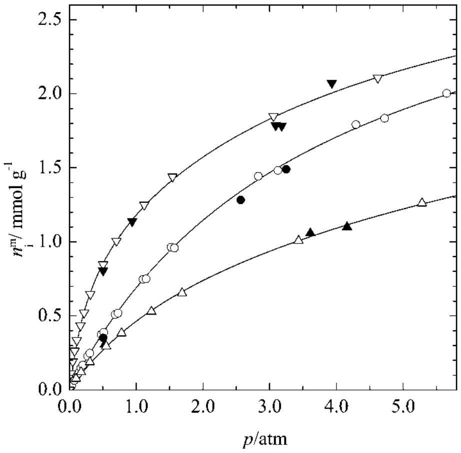

Figure 2. Isotherms measured at 23 °C for pure nitrogen (△), methane (○), and carbon monoxide (▽) on a 5A zeolite. The open symbols are data obtained from standard volumetric expansion experiments and the filled symbols are data measured by gas-phase NMR.[7] The solid lines represent the best correlation available for these data using the dual-site Langmuir (DSL) model.

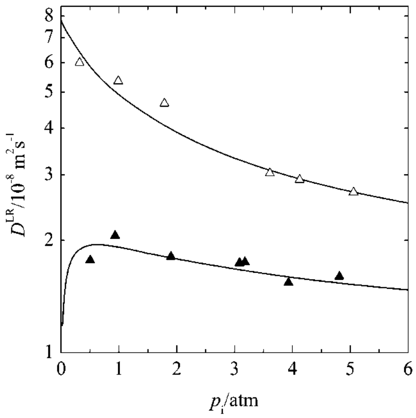

Figure 3. Long-range self-diffusion coefficients for pure nitrogen (△) and carbon monoxide (▼) as a function of pressure. The solid lines are correlations of the experimental data with the LRDM. The tortuosity factors obtained are 2.7 and 2.6 for N_2 and CO, respectively, and reveal that the tortuosity is characteristic of the adsorbent and adsorbate independent.

NMR technique introduced by Kating et al.,[8] a further refinement has been made so that no internal standard is required.[7]

Predictions of D_i^{LR} are performed for transport within idealized cylindrical pores, as are predictions from other models, e.g. the Dusty Gas model.[9] Although the general trends of these predictions should follow experimental data well, the experimental diffusion coefficients are expected to be lower due to the effect of tortuosity.[3] In Figure 3 we compare the self-diffusion coefficients of nitrogen and carbon monoxide within the same 5A zeolite.

The data reveal that the more strongly adsorbed gas, i.e., carbon monoxide, exhibits a lower (long-range) diffusivity than nitrogen, as is intuitively expected and is predicted from LRDM. A higher energetic gas−solid interaction leads to a lower population of gas molecules in the intercrystalline space for CO and therefore to lower values of p^{inter} and consequently, D^{LR}. The predicted maximum in the long-range diffusion coefficients of CO with increasing pressure was initially a surprising result to us. Intuitively one expects that the increased number of collisions a gas molecule experiences as pressure increases would lead to smaller diffusion coefficients. Indeed this is true for the pressure dependence of D_i^{inter}. In contrast, as the pressure is reduced D_i^{inter} increases until the Knudsen limit is reached at which point D_i^{inter} remains constant. To understand the maximum in D_i^{LR} vs P_i one must recall that D_i^{LR} is affected not only by the pressure dependence of D_i^{inter} but by that of p_i^{inter} as well. At low pressures n_i^m is directly proportional to p_i (Henry's law region) and, by eq 1, p_i^{inter} is expected to be independent of pressure. Outside of the Henry's limit the ratio n_i^m/p is less than the Henry's constant (for a Type I isotherm) and thus p_i^{inter} increases with increasing pressure. The opposing dependence of D_i^{inter} and p_i^{inter} with increasing pressure, therefore, can give rise to a maximum in the value of D_i^{LR}. Since D_i^{inter} and p_i^{inter} approach constant values in the low-pressure limit as the Knudsen and Henry's law regimes are reached, D_i^{LR} is also predicted to become independent of pressure in this pressure region.

Table 1. Long-Range Self-Diffusion Coefficients for a Ternary Gas Mixture within a 5A Adsorbent[a]

	$D(N_2)$/ (10^{-8} m^2 s^{-1})	$D(CH_4)$/ (10^{-8} m^2 s^{-1})	D(CO)/ (10^{-8} m^2 s^{-1})
experimental	7.3	2.7	1.1
predicted	6.7	2.3	0.99

[a] The gas partial pressures were 2.4, 2.2, and 2.8 atm for N_2, CH_4, and CO, respectively, and the respective loadings were 0.14, 0.48, and 1.4 mmol g^{-1}. Predictions were made using the LRDM with use of the tortuosity factors determined from pure adsorbate/adsorbent systems.

We have also investigated the diffusion of a ternary gas mixture within the same 5A adsorbent. Here, the gas-phase NMR technique has been applied in order to obtain the accurate surface excess for the multicomponent gas mixture. In Table 1 we compare our experimental results with predictions based on the LRDM. Clearly the predictions are in good agreement with the experimental data.

For comparison, the diffusion coefficients of the *pure* gases within the 5A sample at the corresponding partial pressure are predicted (and experimentally found) to be 2 to 3 times greater than within the mixture. This result clearly reveals that the additional molecular collisions within a multicomponent system significantly reduce overall diffusion rates.

In summary, we have demonstrated that the long-range diffusivity within zeolite pellets can be accurately described by the LRDM when isotherm and porosity data are available. From comparisons of the model with experimental data we obtain tortuosity factors that can be used to predict self-diffusion within multicomponent (binary and ternary)[2] gas mixtures very well. Additional experimental results (not shown here) reveal that the LRDM can accurately predict self-diffusion behavior while simultaneously varying pressure, temperature, and sorbate loading.[2]

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