

**LONG-RANGE DIFFUSION IN BEDS OF NANOPOROUS PARTICLES: PITFALLS  
AND POTENTIALS**

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## **Abstract**

Owing to the recent progress in the area of hardware and software of the PFG NMR technique molecular transport in real-life zeolite systems, such as zeolite beds and particles of formulated fluid catalytic cracking (FCC) catalysts, can be investigated in detail. These studies have revealed a number of important features of molecular transport in zeolites, which are reviewed in the present paper. In particular, the anomalous character of intracrystalline diffusion in MFI-type zeolites, dependence of the tortuosity factor in zeolite beds on diffusion regime, and the role of various modes of diffusion in transport limitations arising for catalytic reactions in FCC catalysts will be discussed.

## 1. Introduction

Optimization of zeolites for various industrial applications, such as large-scale separations and catalysis, requires understanding of the transport of guest molecules. Intracrystalline transport in zeolite single crystals with the ideal structure has been the subject of a large number of recent theoretical and experimental studies [1-8]. However, the knowledge on molecular transport obtained from these studies often cannot be directly applied for real-world zeolites used in industry. This happens mainly due to the following two reasons. The first one is related to the fact that primary zeolite particles used in industrial applications are usually not single crystals. These particles may often be described as agglomerates of crystallites containing large amounts of various structural defects. Secondly, due to the small size of primary zeolite particles, they are usually used in the form of beds, pellets or membranes. Transport properties of such macroscopic systems may obviously be quite different from those of zeolite single crystals [1,2,4,5,8]. In comparison to intracrystalline diffusion in zeolite crystals with the ideal structure, molecular transport in real-life zeolite particles containing various defects as well as long-range diffusion in beds of zeolite particles for displacements, which are much larger than the particle size, have not been sufficiently well investigated. Owing to the ability of monitoring diffusion in an extremely broad range of molecular displacements, pulsed field gradient (PFG) NMR has all the potentials to overcome these deficiencies in our knowledge. This will be demonstrated in the present work. It will be shown that the combined application of PFG NMR and dynamic Monte Carlo (MC) simulations presents an especially powerful approach, which allows obtaining quantitative information on transport and structural properties of real-world zeolite systems.

The rest of the paper will be organized as follows: in the second section we will present results of the investigation of the influence of structural defects on molecular transport in MFI-type zeolite crystals. In the third section some new, interesting aspects of long-range diffusion in beds of zeolite crystals will be discussed. In the fourth section selected results of the PFG NMR study of molecular transport in particles of industrial fluid catalytic cracking (FCC) catalysts will be described. Finally, we will give some concluding remarks in the last section.

## 2. Intracrystalline transport barriers in MFI-type zeolites

Recent improvements of the hardware and software of our PFG NMR spectrometers [9] have allowed us to carry out diffusion measurements in MFI-type zeolites over a wide range of diffusion times and temperatures [10]. The reliability of the measured data has been significantly improved due to application of the 13-interval PFG pulse sequence [11]. Under our experimental conditions this sequence allows eliminating the disturbing influence of magnetic field inhomogeneities, which are also known as internal magnetic field gradients, by making use of alternating (bipolar) pulsed field gradients. Internal gradients are induced by the susceptibility variations in heterogeneous samples.

The diffusivities of guest molecules measured in MFI-type zeolites at low temperatures were found to decrease progressively with increasing root mean square displacements (Fig. 1a,b) [10].

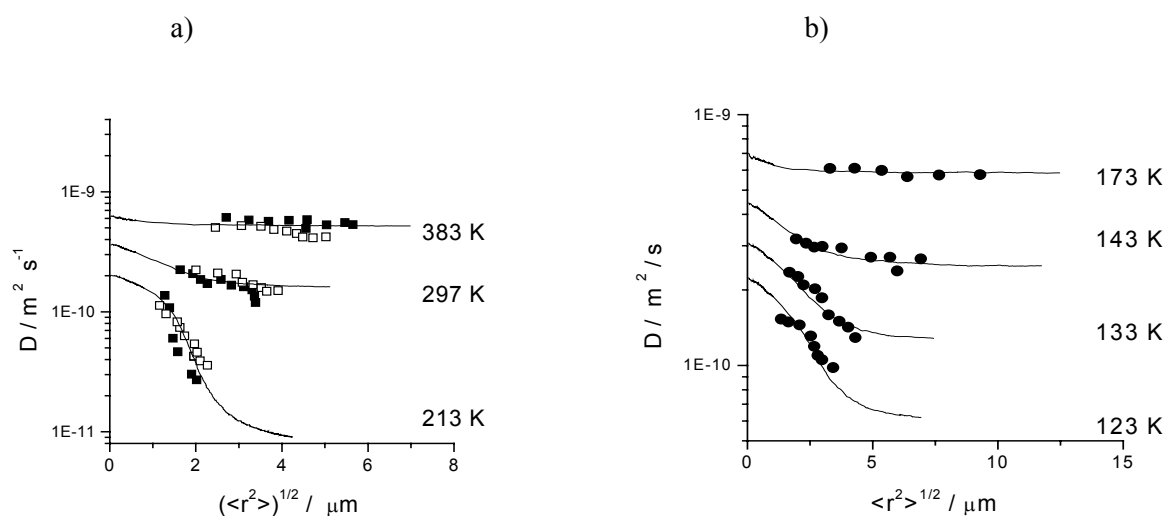


Fig.1 Dependencies of the diffusion coefficients on the root mean square displacements at different temperatures measured by using PFG NMR (points) and determined by dynamic MC simulations (lines): (a) for n-butane in silicalite-1; (b) for methane in ZSM-5.

Under our experimental conditions, the root mean square displacements were always sufficiently small in comparison with the size of the crystals so that the effect of diffusion restriction by the outer surface of the crystal was negligible. The dependencies in Fig.1 have been attributed to the existence of intracrystalline

transport barriers [10,12]. Transport barriers are expected to give rise to correlations in the movements of individual molecules on the length scale comparable with the mean separation between these barriers. In this case, in contrast to the Einstein's equation, the measured intracrystalline diffusivities of guest molecules may decrease with increasing root mean square displacement, as has been observed experimentally (Fig.1). It is essential to note that the internal pore structure of MFI-type zeolites is known to give rise to anisotropic diffusion [1]. Hence, the diffusivities in Fig.1 are in fact one third of the trace of the diffusion tensor

$$D = \frac{1}{3}(D_x + D_y + D_z) \quad (1)$$

It is seen in Fig.1 that for the same values of the root mean square displacements the relative changes of the diffusivities at low temperatures are much more pronounced than at high temperatures. Such a behavior may be easily explained by assuming that the activation energy of barrier permeation substantially exceeds that of diffusion through the unperturbed zeolite. Fitting the experimental dependencies in Fig.1 by the results of the dynamic MC simulations we have obtained the values of 26.5 kJ/mol and 13.8 kJ/mol for the activation energy of the barrier permeation ( $E_b$ ) for n-butane in silicalite-1 and for methane in ZSM-5, respectively [12]. At the same time, the activation energy of diffusion in the limiting case of small displacements, i.e. in the lattice free of intracrystalline transport barriers, was found to be  $E_d = 5.0$  kJ/mol for n-butane in silicalite-1 and  $E_d = 3.8$  kJ/mol for methane in ZSM-5 [12]. These latter values are in satisfactory agreement with those measured at short diffusion times by PFG NMR and Quasi-Elastic Neutron Scattering (8.1 kJ/mol for n-butane in silicalite-1 and 4.5 kJ/mol for methane in ZSM-5) [1,13,14]. The dynamic MC simulations were carried out on a cubic lattice assuming (i) equal barrier spacing along all three crystallographic directions and (ii) the same activation energy of the barrier permeation for all the barriers. The information about the influence of the MFI-type topology on diffusion (i.e. of the diffusion anisotropy) was preserved by using different hopping rates for different crystallographic directions.

The characteristic distance between the transport barriers determined from the fitting of the experimental data by dynamic MC simulations in the crystals with the size of up to  $250 \times 100 \times 100 \text{ } \mu\text{m}^3$  has been found to

be in the range of several microns [12]. These data suggest that large MFI-type crystals are inhomogeneous on the length scale, which is an order of magnitude smaller than the crystal size but, at the same time, orders of magnitude larger than the size of the elementary building units of the crystals (several nanometers [15]). Most recent results of atomic force microscopy investigation of large silicalite-1 crystals [16] seem to confirm the existence of structural inhomogeneities on the length scale comparable with that of the barrier separation. The data presented in Ref.16 indicate that, similar to many other zeolites [17], MFI-type crystals grow via the deposition and subsequent expansion of layers. An occurrence of structural defects in the layers may become an impediment in the layer propagation. As a result, a build up of the layers leading to the formation of the experimentally observed terraces with a height of up to 110 nm [16] may occur. Such terraces can propagate through the whole crystal because the affected layers also propagate through the whole crystal. In our opinion such defects present a very likely candidate for the structural origin of the above discussed intracrystalline transport barriers.

### **3. Long-range diffusion in zeolite beds**

#### **3.1. Common approach in the description of intracrystalline and long-range diffusion**

The presence of strong adsorption sites, such as acid sites or defects, in the pore systems of many zeolites may result in a bimodal distribution of the residence time of guest molecules (viz. the time spent at any particular adsorption site during the diffusion process), which includes long residence times on strong adsorption sites and much shorter residence times in the rest of the zeolite lattice. One of the well-known examples of guest-host systems, which may exhibit such property, is ammonia in zeolite H-ZSM-5. The mean residence time of ammonia on acid sites can be expected to be much larger than that on the other, i.e. less attractive (“mobile”) lattice sites. Assuming (i) fast molecular exchange between different sites on the time scale of PFG NMR diffusion measurements (several milliseconds), and (ii) that the product ( $p_s D_s$ ) of the effective diffusivity of the molecules residing on the strong adsorption sites ( $D_s$ ) and the fraction of the molecules on these sites ( $p_s$ ) is negligibly small in comparison to the corresponding product ( $p_m D_m$ ) for the molecules residing on the “mobile” sites, the effective self-diffusion coefficient of ammonia in H-ZSM-5 can be presented as [18]

$$D_{eff} \approx p_m D_m = \frac{N - N_s}{N} D_m, \quad (2)$$

where  $p_m$ , and  $D_m$  are the relative fraction and the diffusivity of the molecules residing on the “mobile” sites of the lattice,  $N$  denotes the number of ammonia molecules and  $N_s$  is the number of the strong adsorption sites in the lattice. Fig.2 demonstrates good agreement between the concentration dependence of ammonia diffusivity measured by PFG NMR and that calculated by using Eq.2 with the best-fit values for  $N_s = 0.829 \pm 0.037$  mmol/g and for  $D_m = (2.3 \pm 0.19) \times 10^{-9}$  m<sup>2</sup>/s [18]. These values were found to be in excellent agreement with the concentration of the acid sites in our sample (0.83 mmol/g) and the diffusivity in defect-free silicalite-1 ( $10^{-9}$  m<sup>2</sup>/s) [19], respectively. The latter diffusivity may be regarded as the diffusivity in the MFI-type zeolite free of acid and defect sites. Consequently, it shall coincide with  $D_m$ .

PFG NMR can be applied to monitor molecular displacements in zeolite beds on a length scale, which is much larger than the size of individual crystallites. The diffusivities recorded under such conditions are usually referred to as long-range diffusivities. The situation arising in this case is similar to that for the intracrystalline diffusion in zeolites with strong adsorption sites. In both cases one can distinguish between two different types of domains with different mobility.

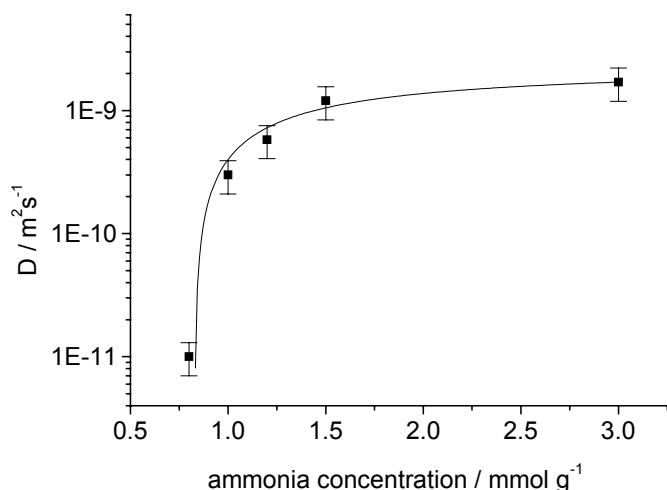


Fig.2. Concentration dependence of the self-diffusion coefficient of ammonia in H-ZSM-5 measured by PFG NMR at T = 298 K. The line shows the best fit using Eq.2.

In the case of long-range diffusion these domains are the intracrystalline volume and the pore system formed by the gaps between the particles of the bed. In complete analogy with Eq.2 one can write for the long-range self-diffusion coefficient [1,20]

$$D_{\text{long-range}} \approx p_{\text{inter}} D_{\text{inter}}, \quad (3)$$

where  $p_{\text{inter}}$  and  $D_{\text{inter}}$  are the fraction and the self-diffusion coefficient in the intercrystalline volume of the bed, respectively. Eq.3 is a direct consequence of the fact that in zeolite beds  $p_{\text{inter}}D_{\text{inter}}$  is usually significantly larger than the diffusivity in zeolite crystals. PFG NMR studies of long-range diffusion in zeolite beds have revealed one important and, at first glance, unexpected property of the tortuosity factor, which will be discussed in the next subsection.

### 3.2 Different tortuosity factors in the Knudsen and gas regime

#### a) Single-component diffusion

Intercrystalline diffusivity of gas molecules in the general case of any particular gas concentration can be presented as the sum of the diffusion resistances associated with molecule-solid and molecule-molecule collisions

$$\frac{1}{D_{\text{inter}}} = \frac{1}{D_{\text{K}}} + \frac{1}{D_{\text{g}}}, \quad (4)$$

where  $D_{\text{K}}$  and  $D_{\text{g}}$  are the Knudsen and gas diffusivities.  $D_{\text{K}}$  and  $D_{\text{g}}$  can be presented in terms of a tortuosity factor, which accounts for the differences between these diffusivities and the corresponding reference diffusivities

$$D_{\text{K}} = \frac{1}{\eta_{\text{K}}} D_{0\text{K}}, \quad D_{\text{g}} = \frac{1}{\eta_{\text{g}}} D_{0\text{g}}, \quad (5)$$

where  $\eta_{\text{K}}$ ,  $D_{0\text{K}}$  and  $\eta_{\text{g}}$ ,  $D_{0\text{g}}$  are the tortuosity factors and the reference diffusivities in the Knudsen and in the gas regimes, respectively. The reference diffusivity in the Knudsen regime is usually defined as that in straight parallel non-overlapping cylindrical pores of infinite length with a diameter equal to the mean intercept length ( $d$ ) in the considered real pore structure



$$D_{0K} = \frac{1}{3} \bar{u} d, \quad (6)$$

where  $\bar{u} = \left( \frac{8RT}{\pi M} \right)^{1/2}$  is a mean thermal speed,  $R$  is the gas constant,  $M$  is the molar mass and  $T$  is the absolute temperature. The reference diffusivity in the gas regime is given by

$$D_{0g} = \frac{1}{3} \bar{u} \lambda, \quad (7)$$

where  $\lambda$  is the molecular mean free path. The value of the mean free path can be calculated as

$$\lambda = \frac{kT}{\sqrt{2} p \pi \sigma^2},$$
 where  $\sigma$  is the critical molecular diameter,  $p$  is the gas pressure and  $k$  is the

Boltzmann constant.

Using Eq.3 PFG NMR diffusion measurements in zeolite beds may be used to probe gas diffusion in the intercrystalline volume of the bed. A great advantage of such measurements in comparison to measurements in beds of non-adsorbing particles is related to the fact that all gas molecules in the sample, including the molecules, which at any given time are adsorbed in zeolite, contribute to the measured NMR signal. This allows performing PFG NMR measurements under extremely broad gas pressure ranges, which cover the regimes of both Knudsen and gas diffusion. In comparison, the NMR signal of gas molecules in beds of non-adsorbing particles is, as a rule, too weak to be measured at the low gas pressures required for the Knudsen regime.

Refs.21,22 report the results of the PFG NMR measurements of the long-range diffusivity of ethane in beds of NaX zeolite with a mean crystal size at around 30  $\mu\text{m}$ . The diffusion measurements were performed in a wide temperature range in order to probe both the gas and the Knudsen diffusion regimes. The transition from the Knudsen to the gas regime occurs with increasing temperature as a consequence of the temperature dependence of the relative fractions of the molecules in the intercrystalline volume of the bed and in the zeolite crystals. The tortuosity factors have been determined by applying Eqs.3-5 to the measured  $D_{\text{long-range}}$  and the calculated  $D_{0K}$  and  $D_{0g}$ . The values of  $D_{0K}$  and  $D_{0g}$  have been calculated by

using Eqs.6,7. Large experimental uncertainties of the estimates of the bed porosity and of the mean crystal size have resulted in a poor accuracy of the estimate of the mean intercept length. This has led to a large uncertainty in the value obtained for the tortuosity factor in the Knudsen regime. Surprisingly, even the lower limit of this value, which has been determined by taking into account the experimental uncertainty, was found to be around 4 times larger than that of the tortuosity factor in the gas regime [21,22]. This is the first direct experimental finding, which implies that the apparent tortuosity factor in the Knudsen regime may be significantly larger than that in the gas regime for one and the same porous medium. Most recent results of dynamic MC simulations have confirmed this conclusion [23]. In these simulations the experimental data on the properties of the studied NaX bed were used as an input to model the experimental system. The zeolite bed has been modeled by using particle-based reconstruction of 58 octahedral particles. The simulations have been performed with molecules moving with a constant velocity, which is equal to the mean thermal speed. The zeolite particles were assumed to be impenetrable for gas molecules. The new directions for molecular trajectories after collisions with the particle surface were calculated using the cosine law of reflection. The results of the simulations have revealed tortuosity factors, which are larger in the Knudsen than in the gas regime [23], thus confirming the experimental results (Table 1). The difference between the ratios of the tortuosity factors in the two regimes obtained by the measurements and by the simulations (Table 1) may be related to the simplified presentation of the diffusion process and of the zeolite bed in the simulations. Larger tortuosity factors in the Knudsen than in the gas regime were also recently obtained by dynamic MC simulations of gas diffusion in various non-zeolitic porous model systems [24,25].

Table 1. Ratios of the tortuosity factors in the Knudsen and in the gas regime obtained for intercrystalline diffusion in the bed of NaX zeolite. The values of the ratios have been obtained by using the results of PFG NMR diffusion measurements [21,22] and of dynamic MC simulations [23].

	PFG NMR measurements	Dynamic MC simulations
$\eta_K/\eta_g$	$\geq 4.0$	2.0

The observed differences between the tortuosity factors in the gas and Knudsen regimes may have their origin in the different influence of the geometrical details of the pore surface of the intercrystalline space on diffusion in these two regimes.

*a) Two-component diffusion*

The description of long-range diffusion in zeolite beds for single-component adsorbate may be extended to the case of the diffusion of two or more different components of adsorbate molecules [26]. For diffusion in the gas regime the long-range diffusivity of the component (*i*) in a multi-component system may be written using Eqs.3-5,7 as

$$D_{\text{long-range}}^i = P_{\text{inter}}^i \frac{1}{\eta_g} \frac{1}{3} \bar{u}^i \lambda^i, \quad (8)$$

where index (*i*) stands for the component (*i*). Similar to the case with one-component adsorbate,  $P_{\text{inter}}^i$  ( $P_{\text{inter}}^i \ll 1$ ) is directly proportional to the partial pressure ( $p^i$ ) of the component (*i*) in the intercrystalline volume. At the same time,  $\lambda^i$  is inversely proportional to the total pressure in this volume (viz. the sum of the partial pressures of all adsorbate components  $p_{\text{total}} = \sum_k p^k$ ). This implies that the long-range diffusivity of the component (*i*) in the gas regime may decrease with increasing temperature when the ratio  $p_i/p_{\text{total}}$  decreases. Let us consider the simplest case of a zeolite bed loaded with two different adsorbates (*i*) and (*j*) ( $P_{\text{inter}}^i \ll 1$ ,  $P_{\text{inter}}^j \ll 1$ ). Assuming for both components (i) the applicability of the ideal gas law and, (ii) the applicability of the Henry law ( $c^k = K^k p^k$ ,  $K^k = K_0^k \exp\left(\frac{Q^k}{RT}\right)$ , where  $c^k$ ,  $K^k$  and  $Q^k$  are, respectively, the intracrystalline concentration, the Henry constant and the heat of adsorption for component ( $k = (i) \text{ or } (j)$ ), one can obtain using Eqs.3-8

$$D_{\text{long-range}}^i \approx \frac{\bar{u} V_{\text{inter}}}{3\sqrt{2}\pi N_A \eta_b \sigma^2 n^i} \left( \frac{1}{1 + \frac{n^j R T K^i V_{\text{int ra}} / V_{\text{inter}}}{n^i R T K^j V_{\text{int ra}} / V_{\text{inter}}}} \right) \approx \frac{\bar{u} V_{\text{inter}}}{3\sqrt{2}\pi N_A \eta_b \sigma^2 n^j} \left( \frac{K_0^j}{K_0^i} \right) \exp\left(\frac{Q^j - Q^i}{RT}\right) \quad (9)$$

where  $n^i$ ,  $n^j$  represent, respectively, the number of moles of adsorbate ( $i$ ) and ( $j$ ) in the bed,  $V_{intra}$ ,  $V_{inter}$  denote, respectively, the total volume of zeolite crystals and the intercrystalline volume of the bed,  $N_A$  is Avogadro's number. The right part of Eq.9 was written using the assumption that  $n^j/K^j \propto p_j \gg p_i \propto n^i/K^i$ . Eq.9 indicates that for  $Q^i > Q^j$  the long-range diffusivity of the component ( $i$ ) may rapidly decrease with increasing temperature. Our first attempts to observe experimentally such an anomalous temperature dependence were not successful. As an example, Fig.3 shows the temperature dependencies of the long-range diffusivity of methane in the presence of another component (ethane- $d_6$ ) in the bed of NaX zeolite, which has been discussed above. Points in Fig.3 show the methane diffusivities measured by using  $^1\text{H}$  PFG NMR under conditions, which, assuming that  $\eta_K = \eta_g$ , insure the applicability of Eq.9. The dot line in Fig.3 presents the temperature dependence of the diffusivity of methane calculated by using Eq.9 with  $Q_{methane} = 19$  kJ/mol and  $Q_{ethane} = 28$  kJ/mol [27]. It is seen in Fig.3 that the anomalous behavior of this temperature dependence (viz. decreasing diffusivity with increasing temperature) has not been observed experimentally. The qualitative difference between the theoretical temperature dependence of the diffusivity of methane obtained by using Eq.9 and the corresponding experimental one may be rationalized by assuming that  $\eta_K > \eta_g$ . Under such condition the transition regime between the Knudsen and gas diffusion extends to the range of pressures (see Eqs.4,5), which for  $\eta_K = \eta_g$  would correspond to the regime of gas diffusion. Hence, assuming that  $\eta_K > \eta_g$ , our experimental conditions may correspond to the transition regime rather than to the gas regime. This makes an application of Eq.9 inappropriate. A simple estimate of the temperature dependence of the long-range diffusivity of methane, which was obtained for the transition regime by using the relation of the reciprocal additivity of the Knudsen and gas diffusivities (Eq.4) and by assuming  $\eta_K/\eta_g = 4.0$  [21,22], has been found to be in a qualitative agreement with the experimental data (compare solid line and points in Fig.3).

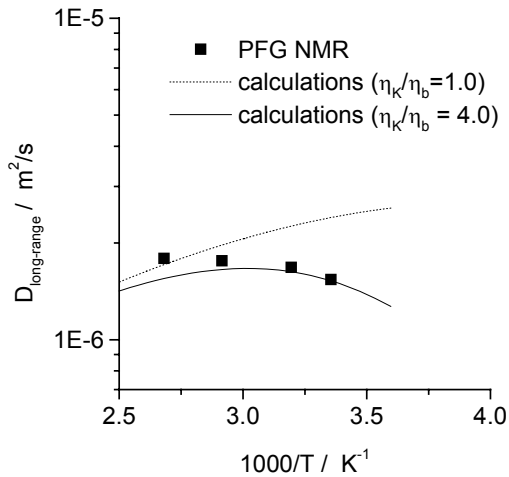


Fig.3 Temperature dependencies of the long-range diffusivity of methane in the presence of another adsorbate component (ethane-d<sub>6</sub>) in the bed of NaX zeolite. The loading levels of methane and of ethane-d<sub>6</sub> correspond to the equilibrium with the mixture of 80 mbar of methane and 80 mbar of ethane-d<sub>6</sub> in the gas phase at 298 K. Under this condition the value of the molecular mean free path ( $\lambda$ ) for methane was estimated to be around 1 micron.

#### 4. Diffusion in particles of industrial FCC catalysts

Recent progress in the area of PFG NMR technique has made possible the direct measurement of diffusivities in industrial FCC catalysts. In the TROCAT project [28] PFG NMR is used to overcome one of the main shortcomings in the optimization of FCC catalyst, i.e. the lack of the optimization with respect to the transport properties.

Typical FCC catalysts consist of particles, which are for the most part made of zeolite crystals and the so-called “matrix”. Along with the nanopore system of zeolite, these particles also possess a complex system of meso- and macropores located in the matrix. PFG NMR has been applied to measure intracrystalline and intraparticle diffusivities of n-octane in FCC catalysts. The latter diffusivity is defined as the diffusion coefficient for displacements, which are much larger than the crystal size, but, at the same time, much

smaller than the particle size. The results of the extrapolation of the measured intracrystalline and intraparticle diffusivities of n-octane to those of larger alkanes ( $> C_{14}$ ) at typical FCC temperatures (500-600 °C) show that for large molecules the rate of molecular exchange between the particles and their surroundings is primarily determined by the intraparticle diffusion coefficient. This suggests that possible transport limitations during FCC catalysis are primarily related to the intraparticle diffusion. An observation of the correlation between the intraparticle diffusivities and the catalytic performance of the FCC catalysts having the same amounts of the same zeolite Y but different macro- and mesopore systems has confirmed this conclusion. Fig.4 shows an example of such a correlation, where the catalytic performance is represented by the conversion to gasoline.

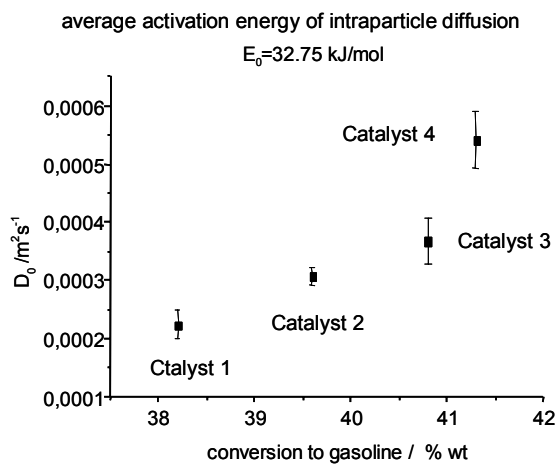


Fig.4 Correlation between the preexponential factor of the intraparticle diffusivity ( $D_0$ ) for n-octane and the conversion to gasoline for the same catalyst-to-oil ratios. The intraparticle diffusivity of n-octane has been presented as  $D_{\text{intra}} = D_0 \exp\left(-\frac{E_0}{RT}\right)$ , where  $E_0$  is the activation energy of intraparticle diffusion.

The activation energy of intraparticle diffusion of n-octane in the catalyst samples (around 33 kJ/mol), which has been obtained from PFG NMR measurements, was found to be in satisfactory agreement with the heat of adsorption of n-octane in these samples. Hence, in complete analogy to the long-range diffusion in zeolite beds in the Knudsen regime [1,20-22] the temperature dependence of the intraparticle diffusivity appears to be primarily determined by that of the fraction of molecules in the

macro- and mesopores of the particles. Consequently, the model for the long-range diffusion in zeolite beds, which has been discussed in section 3, seems to be applicable to intraparticle diffusion in FCC catalysts where the macro- and mesopore volume of the particles plays the role of the intercrystalline volume in zeolite beds. According to this model the intercrystalline diffusivity in the Knudsen regime, which is expected to hold for n-octane diffusion in FCC catalyst particles at sufficiently small n-octane concentrations, depends on the tortuosity factor and on the mean intercept length in the macro- and mesopore system of the particles (Eqs.4-6). The role of these two parameters in the observed deviations between the values of the intraparticle diffusivities in the catalysts 1,2,3 and 4 in Fig.4 can be evaluated separately by (i) performing PFG NMR measurements of the tortuosity factors for diffusion of liquids in the macro- and mesopore system of the particles, and by (ii) carrying out measurements of the pore size distribution by using NMR cryoporometry [29]. The tortuosity factors can be determined by relating the measured diffusivities of liquids in the particles to the corresponding unrestricted diffusivities in the liquid phase. Noting that the total volume of the zeolite pores in the particles is much smaller than that of the meso- and macropores, it may safely be assumed that the diffusivities of liquids in the particles approach those in the meso- and macropore system. The measurements of the pore size distribution are based on the fact that the melting point of the fluid confined in porous system is progressively decreased for smaller pores [29]. Our preliminary results indicate that the differences between the intraparticle diffusivities shown in Fig.4 are primarily related to the differences in the mean intercept length, which is determined by the pore size distribution.

## **5. Conclusions**

Recent developments in the area of PFG NMR technique allow carrying out detailed studies of molecular diffusion in real-world nano- and microporous materials. The results reviewed in this paper show that the characteristic diffusivities in zeolites might depend on molecular displacements, even when these displacements are much larger than the size of the zeolite unit cell and, at the same time, much smaller than the crystal size. Such dependencies have been attributed to the existence of

intracrystalline structural defects, which may occur in a spatially correlated way facilitated by the crystal growth mechanism by the process of layer addition. PFG NMR studies of long-range diffusion in zeolite beds have provided the first direct experimental evidence that the apparent tortuosity factor in the Knudsen regime of diffusion may be significantly larger than that in the gas regime for one and the same bed. This finding has been recently confirmed by the results of dynamic MC simulations. Studies of molecular diffusion in FCC catalysts have revealed that possible transport limitations during FCC catalysis are primarily related to the intraparticle diffusion, viz. the diffusion for displacements, which are much larger than the crystal size, but, at the same time, much smaller than the size of catalyst particles. As a result of the new knowledge obtained by using PFG NMR, the transport optimization of FCC catalysts can be based on scientific rather than on the conventional “try and see” approach.

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