PFG NMR study of the transport properties of A-type zeolite membranes

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The transport properties of an A-type zeolite membrane are traced by monitoring the diffusion paths of ethane and propane from *ca.* 300 nm up to 10 μm; over distances < 1 μm, the diffusivities are found to be comparable with those in a mono-crystal, while for large displacements by a factor of two to three smaller diffusivities were observed.

Offering a number of most exciting technological advantages in catalysis and gas separation, microporous membranes have become an attractive subject of applied research. Owing to their thermal and chemical stability, among them the inorganic membranes have attained special attention.

Zeolite membranes have recently been made available on a commercial basis and have been shown to be capable of achieving very high levels of separation along with very high permeate fluxes for a range of binary mixtures, for example water removal from methanol, ethanol and isopropyl alcohol.[1] The particular materials used in this study were pieces of membranes that were fragmented during handling. From scanning electron micrographs, these pieces appeared to be crystallite agglomerates with diameters of tens to hundreds of micrometers, where the crystallite diameters were of the order of micrometers.

The membranes were prepared from homogeneous solution with a composition given by the molar ratio 5 SiO_2 : Al_2O_3 : 55.12 Na_2O : 1004.66 H_2O. An aluminate solution was prepared by dissolving small pieces of aluminium wire (Aldrich, 2.4 g) in aqueous NaOH (86.56 g Analytical grade NaOH pellets in 362.46 g distilled water) over a 48 h period. A sodium silicate solution was prepared by dissolving NaOH pellets (80 g) in distilled water (340.4 g) then adding an aqueous silicate solution (BDH, 25.5% SiO_2, 7.5% Na_2O, 40.82 g) with vigorous stirring. After at least 15 min of stirring, the pre-heated aluminate solution was added, and the stirring continued for 5 min. The resultant solution was transferred to a preheated container for membrane preparation. Free-standing samples of zeolite membrane were prepared by placing the above solution in a sealed Teflon container which was placed in an oven at 50 °C for 48 h. The container was removed from the oven, drained and the zeolite film that lightly adhered to the container walls was throughly rinsed with distilled water until the rinsings were pH neutral. Samples of the membrane detached themselves during this procedure and were collected and dried at 70 °C overnight. The material was ion exchanged to the Ca-form by soaking it in 0.1 M $Ca(NO_3)_2$ overnight followed by thorough rinsing in doubly distilled, deionised water. The material was oven-dried at 120 °C for 24 h.

The pulsed field gradient (PFG) NMR method is a bulk technique, which allows the determination of the probability distribution of molecular displacements within the sample.[2,3] The displacements, which may be resolved by this technique are in the range of micrometers, with observation times of typically milliseconds.

For the preparation of the PFG NMR samples, the zeolite material was filled into glass tubes of 7.5 mm o.d. and activated by heating at a rate of 10 K h^{-1} under continuous pumping up to a final temperature of 400 °C, where it was kept for 10 h. After cooling to room temperature the probe molecules (the 'diffusants') were introduced by chilling from a calibrated gas volume with a set pressure. The amount adsorbed was afterwards checked by measuring the intensity of the NMR signal.

The diffusion measurements have been carried out by means of the home-built PFG NMR spectrometer FEGRIS 400 at a proton resonance frequency of 400 MHz with magnetic field gradient amplitudes up to 24 T m^{-1}.[3,4] The attenuation of the

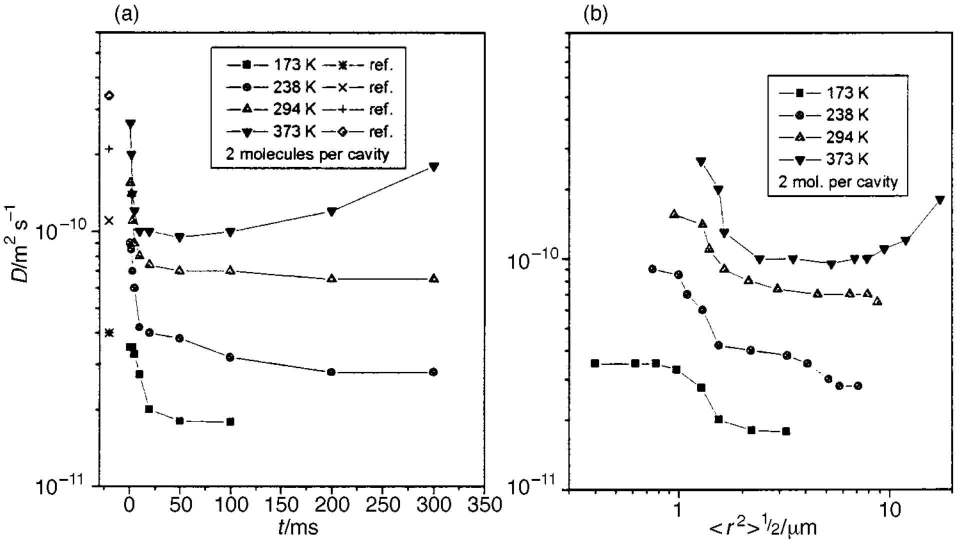

Fig. 1 (a) Ethane diffusivity in NaCaA membrane as a function of the observation time at different temperatures; ref.: results of previous PFG NMR studies with crystalline zeolite NaCaA. (b) Ethane diffusivities in NaCaA membrane as a function of the root mean square displacement at different temperatures.

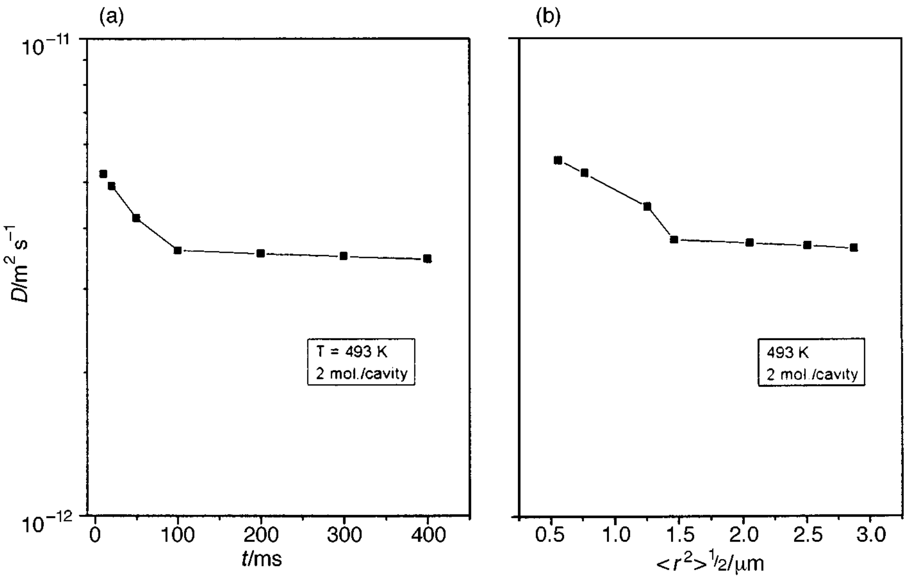

Fig. 2 (a) Propane diffusivity in NaCaA membrane: (a) as a function of the observation time and (b) as a function of the root mean square displacement.

NMR signal (the 'spin echo') *versus* the squared gradient amplitude was essentially found to follow a monoexponential decay, as to be expected for normal diffusion in a quasihomogeneous medium. The effective diffusivity was determined by comparing the signal decay with that of a standard [water, $D = (2.04 \pm 0.08) \times 10^{-9}$ m^2 s^{-1} at 20 °C].[5] It is defined as the ratio

$$D = \langle r^2(t) \rangle / 6t \qquad (1)$$

between the mean square displacement and the observation time.

Fig. 1(a) shows the dependence of the ethane diffusivity in the zeolite membrane at a loading of two molecules per cavity for different temperatures. For comparison, the diffusivity data of previous PFG NMR studies[6] with ethane in NaCaA zeolite crystallites are also included. It appears that these data are in reasonably good agreement with the results of the present study for sufficiently short observation times. The information provided by these studies becomes more obvious in the representation of the diffusivities *versus* the covered displacements [Fig. 1(b)]. There is a pronounced decay for displacements around 1 μm, which should be attributed to transport resistances, most likely situated at the interfaces between the individual crystallites. For shorter displacements, the majority of the diffusants do not interfer with these barriers; one is able to trace the true intracrystalline diffusion. For larger displacements, the molecules repeatedly have to overcome these transport resistances. This leads to a slight reduction of the diffusivity. The enhancement observed in the high-temperature case for displacements > *ca.* 10 μm may be associated with the occurence of long-range diffusion, when more and more molecules are able to get out of the zeolite bulk phase, either through cracks in the material or through the outer surface of the membrane particles.

As a consequence of the substantially lower mobility, propane in NaCaA offers much poorer measuring conditions. The most reliable measurements for this system have therefore been carried out at 493 K, the highest temperature accessible with our device. Fig. 2(a) and (b) represent the corresponding diffusivity data. Similarly as with ethane, for molecular displacements < *ca.* 1 μm, there is an increase in the diffusivities, which should be a consequence of unrestricted diffusion for displacements sufficiently small in comparison with the crystallite radii. It should be mentioned that previously measured diffusivities of propane in NaCaA zeolite crystallites under the same measuring conditions revealed slightly lower values (2.5×10^{-12} m^2 s^{-1}).[6] It is possible that the difference to the value which in the present studies is assumed to be the true intracrystallite one, is caused by slight differences in the degree of calcium exchange. Such differences should be much more significant for propane than for ethane having a smaller critical diameter.

To our knowledge, in these investigations, for the first time transition resistances between the individual crystalline compartments in nanoporous membranes have been probed microscopically. For the considered probe molecules (ethane, propane) a notable transport resistance was observed, which, however, was found to be much smaller than the surface resistance on isolated NaCaA type crystallites.[7] Further experimental evidence is required to decide whether the observed behaviour is a general feature of polycrystalline membranes.

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