Measurement of the Diffusivity of Benzene in Microporous Silica by Quasi-Elastic Neutron Scattering and NMR Pulsed-Field Gradient Technique

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Abstract. The diffusivity of benzene in a microporous silica powder has been measured by neutron scattering and NMR techniques. The measurements have been performed on un-supported silica but the powder has the same characteristics as the active layer of a real membrane. Self-diffusion coefficients of the order of $10^{-10}\,\mathrm{m^2 s^{-1}}$ are found at 300 K by both techniques so that the model of Knudsen diffusion is not valid for benzene in this microporous material. Due to the presence of small pores, the diffusion of benzene in the membrane-material approaches the diffusion regime usually observed in zeolites. Furthermore, the diffusivity of benzene follows an Arrhenius law with an activation energy of 11 kJ mol^{-1}.

Introduction

In recent years, the preparation of inorganic microporous membranes has been intensively investigated. Important applications of these materials are foreseen for gas separation and catalysis. Their properties are well suited for severe separation conditions, unlike organic polymer membranes which have low chemical and thermal resistance. For industrial applications, the active membrane (e.g., alumina or silica) is deposited onto a macroporous ceramic support, the thickness of the membrane being of the order of a few μm.

To prepare microporous membranes (diameter of the pore <2 nm), sol-gel techniques are used to obtain homogeneous materials. It is possible to design the microstructure of the systems (pore size, porosity, surface area) by controlled hydrolysis and condensation of alkoxides (Julbe et al., 1993). For catalytic applications, the membrane can be used as a catalyst or as a support for metal particles to perform simultaneously

the reaction and the separation of the products (Armor and Noble, 1993). One of the classical examples is the dehydrogenation reaction of cyclohexane to benzene. In order to obtain high levels of conversion, hydrogen must diffuse much faster than the other components. This implies that the diffusion coefficient of benzene should be several orders of magnitude smaller than the Knudsen diffusivity usually found in mesoporous systems. The situation is comparable to the diffusion in zeolites where the size of the molecule relative to the size of the pore is critical. The experimental determination of diffusion coefficients in microporous membranes is thus essential to master the transport properties of these materials. Furthermore, mathematical modelling of membrane reactors requires reasonable values of the diffusion coefficients to make useful predictions of performance.

The measurement of diffusion coefficients in microporous materials is however not straightforward. In the field of zeolites, reported diffusion coefficients for

a given molecule in similar structures may differ by several orders of magnitude according to different techniques (Caro et al., 1993). We have applied quasi-elastic neutron scattering (QENS) and pulsed-field gradient NMR (PFG NMR) methods to study the diffusivity of benzene in a microporous silica powder at different loadings and temperatures. All our measurements are performed with non-supported silica but the same material is used to prepare silica membranes. Since the QENS and PFG NMR experiments are made under equilibrium conditions, i.e., without a pressure drop, care should be taken before comparison with permeability data (Kärger and Ruthven, 1992). This work represents the first series of microscopic measurements reported so far for this type of system.

Experimental

Non-supported silica was prepared by the sol-gel process using a silicon alkoxide precursor. An organic binder was added to the sol to control its rheological behavior. This binder is responsible for the open microporous structure of the membrane-material. The sol was deposited and dried on an aluminium foil. The thin non-supported film was cut into small pieces, the smallest dimension being the thickness which was found by electron microscopy to be of the order of 50 μm. The organic binder was eliminated under flowing oxygen at 720 K. For the neutron measurements, this operation was repeated several times in order to prepare several grams of dried powder. The silica powder was characterized by N_2 adsorption-desorption isotherms and by small-angle X-ray scattering (SAXS). The nitrogen adsorption isotherm was characteristic of microporous materials. The pore size distribution obtained by the MP method (Mikhail et al., 1968) shows several peaks below 2 nm (in diameter) and the BET surface area is of 600 m^2g^{-1}. The SAXS data were analysed using the multiple scattering theory (Renouprez et al., 1985). A narrow pore size distribution with a mean diameter of 1.8 nm was determined by this technique (Fig. 1), assuming spherical pores. The surface area calculated using the Porod law is of 1600 m^2g^{-1}. The value of the surface area obtained by SAXS is larger because of small micropores and because with this technique one measures the corrugation on the atomic scale.

The neutron experiments were performed at the Rutherford Appleton Laboratory, UK, using the spectrometer IRIS (Carlile and Adams, 1992). This instrument is a high-resolution inverted-geometry
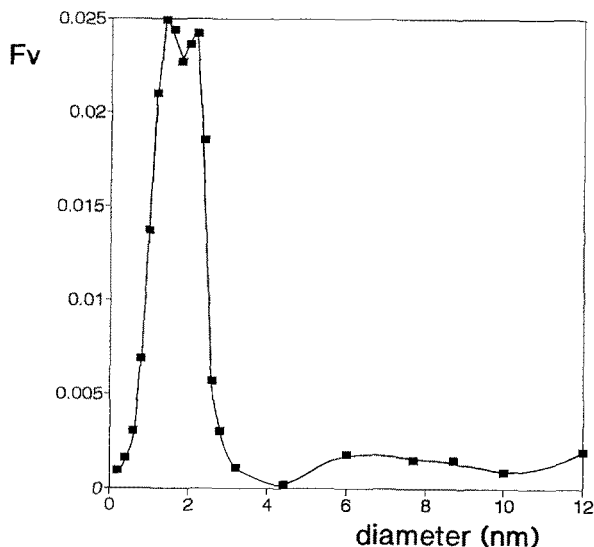

Fig. 1. Pore size distribution obtained by SAXS for microporous silica.

spectrometer with graphite and mica analysers giving elastic resolutions in the range 1–50 μeV. The silica powder ($\approx$1 g for each sample) was contained in thin-walled aluminium containers of circular geometry. Other samples were prepared by adsorbing known amounts of benzene on the silica powder, before the transfer in the containers. Results for liquid benzene were also obtained using a similar container (thickness of the liquid: 0.6 mm).

The NMR measurements were made on the spectrometer FEGRIS at the Department of Physics of the University of Leipzig (Kärger et al., 1988). The silica samples were contained in glass tubes of diameter 7 mm. The benzene loadings were the same for the NMR and for the neutron experiments; θ_1 corresponds to 0.09 g of benzene per g of silica and θ_2 to 0.14 g/g, which is close to saturation.

Results

Quasi-elastic Neutron Scattering

After scattering by the sample, neutrons are analysed as a function of time and angle: the time-of-flight of the scattered neutrons is related to their energy transfer, $\hbar\omega$, and the scattering angle to the momentum transfer, $\hbar Q$. A total of 51 spectra are recorded simultaneously, covering scattering angles ranging from 20° to 160°. Groupings of the detectors can be made subsequently to
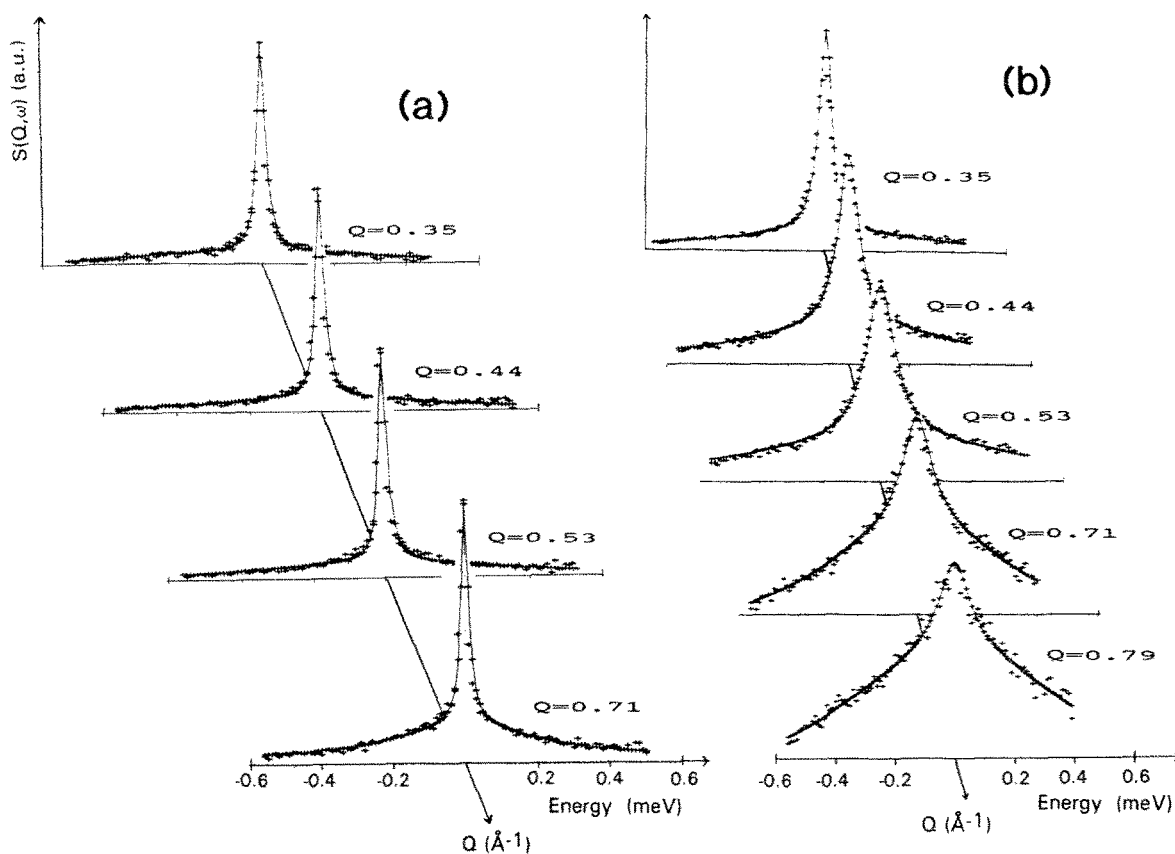
Fig. 2. QENS spectra, obtained at different momentum transfers, of benzene (a) in the silica powder, (b) in the liquid phase (300 K).

improve the statistics. The scattering of the bare powder was recorded at 300 K and was subtracted from the spectra. Corrections were made for the incident neutron spectrum but not for absorption and self-shielding. This is justified by the high transmissions of the samples: 97% for bare silica, 94–96% for benzene-loaded silica, and by the small proportion of absorption. However, the experimental error will be larger than in our previous studies with zeolites, being estimated to 50%. Some experimental spectra obtained at 300 K with the graphite analysers are reported in Fig. 2 for benzene in the silica powder (θ_2) and in the liquid phase. Since the elastic peak broadening is directly related to molecular diffusion, the net effect of microporous silica appears in the reduction of the peak broadening with respect to the free liquid, corresponding to a decrease in the self-diffusion coefficient.

Because of the large incoherent cross section of hydrogen, only this source of scattering needs to be considered. The scattered intensity is related to

self-motions of the hydrogen atoms under the effect of the different molecular motions (Bée). The measured QENS spectra have been fitted simultaneously with a scattering function for translational diffusion convoluted with the uniaxial rotation around the C_6 axis of benzene and with the instrumental resolution. Because of insufficient statistics, it was not possible to detail the diffusion mechanism by applying a jump diffusion model, as was considered in zeolitic systems (Jobic et al., 1992). Therefore, a simple model of Fickian diffusion was used. Calculated energy spectra are compared to experimental ones in Fig. 2, at different Q values. At 300 K, the resulting self-diffusion coefficients are 1.3×10^{-10} m^2s^{-1} for θ_1 and 10^{-10} m^2s^{-1} for θ_2, respectively. Since only two temperatures (300 and 350 K) could be studied, the activation energy which was obtained, 15 kJ mol^{-1}, is merely an approximate estimate. In the liquid phase, the self-diffusion coefficient of benzene at 300 K is 2.5×10^{-9} m^2s^{-1}, in agreement with the literature.
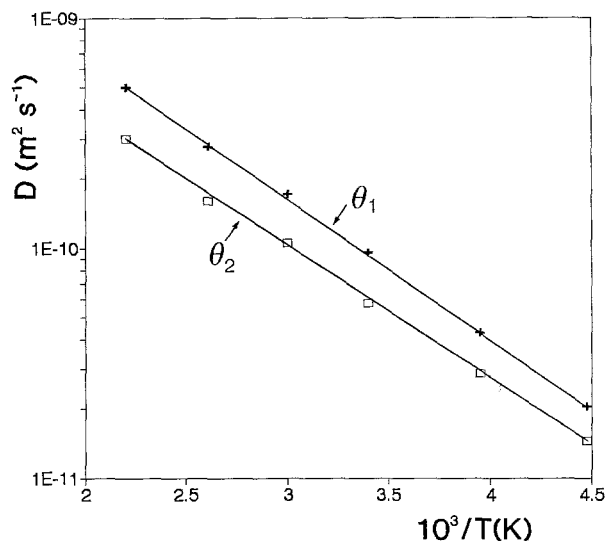
Fig. 3. Arrhenius plots of the PFG NMR self-diffusion coefficients of benzene in the silica powder for the two considered loadings of 0.09 g/g (θ_1) and 0.14 g/g (θ_2).

Pulsed-field Gradient NMR

The dependence of the diffusivities on the observation time has been measured at a few selected temperatures. It has been found that the mean square displacement varied linearly with the observation time, over diffusion paths ranging from 1 to 10 μm, as required for Fickian

diffusion. Since the diffusion path is much smaller than the smallest dimension of the silica film, the measured diffusivities reflect true intrafilm values and are not affected by diffusion between the film cuts. The self-diffusion coefficient obtained at 300 K for θ_1 is 9.5×10^{-11} m^{2}s^{-1} and 5.7×10^{-11} m^{2}s^{-1} for θ_2. Since the experimental error is $\approx$15% compared to 50% for the QENS results, the accuracy of the PFG NMR measurements is better in this study. To derive activation energies, the temperature has been varied between 223 and 453 K for a constant measuring time of 3 ms. An Arrhenius plot of the self-diffusion coefficients thus determined is shown in Fig. 3. For both loadings, an identical activation energy of 11 kJ mol^{-1} has been obtained.

Discussion

The self-diffusion coefficients which are obtained by QENS and PFG NMR for benzene in the silica powder are in good agreement, despite the fact that the mean diffusion paths followed are of different magnitude. In QENS, under the experimental conditions used, molecular diffusion is monitored over a few nm whereas in PFG NMR molecular displacements amount to some μm. Nevertheless, the same Fickian diffusion is observed by both techniques, the diffusion coefficient being of the order of 10^{-10} m^{2}s^{-1} at 300 K. The observed decrease of the diffusion coefficient with increasing
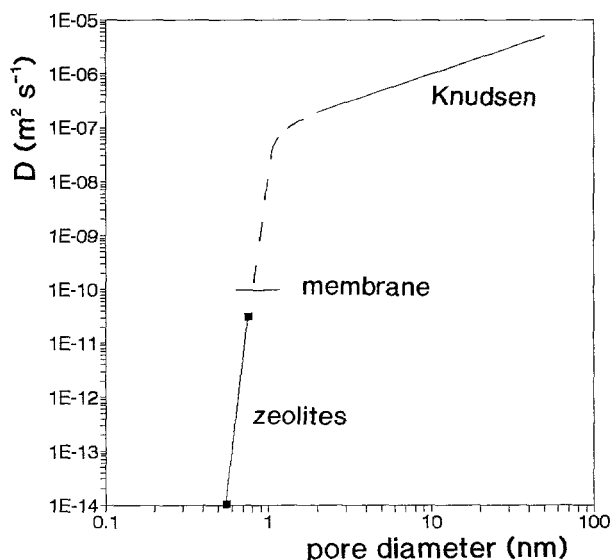

Fig. 4. Diffusion coefficients of benzene, at 300 K, as a function of pore diameter.

concentration may be explained by the mutual hindrance of the molecules (Kärger and Ruthven, 1992).

According to the IUPAC classification, the mean pore size in the silica powder is at the limit between micro- and mesoporous pores. In the mesopores, the model of Knudsen diffusion is usually followed. However for a pore diameter of 2 nm, this model would yield a diffusion coefficient of 2×10^{-7} m^{2}s^{-1} for benzene at 300 K. Since the measured diffusion coefficient is more than 3 orders of magnitude lower than this, the model of Knudsen diffusion is not appropriate. This is illustrated schematically in Fig. 4 which clearly shows two regimes for Knudsen diffusion and for diffusion in zeolites (such a diffusivity pore size diagram was first proposed by Weisz, (Weisz, 1973)). For zeolites, the values obtained at low loadings of benzene in ZSM-5 and in NaX have been considered (Caro et al., 1993; Kärger and Ruthven, 1992). The pore dimensions in ZSM-5 and in NaX are ≈0.55 and 0.75 nm, respectively. It appears that the diffusion of benzene in the silica powder approaches the diffusion regime in zeolites, because of the presence of small pores. Indeed, one has to consider the dimension of the pores between the cavities instead of the diameter of the cavities. The silica powder which has been studied in this work may thus be assumed to have an effective (limiting) pore diameter of the order of 1 nm.

Further, Knudsen diffusivity is only weakly dependent on temperature. In the temperature range studied in PFG NMR, 223–453 K, the variation would be of a factor $\sqrt{2}$ (the diffusivity is proportional to the square root of the temperature), whereas a variation of more than one order of magnitude is observed. The diffusion in this microporous membrane-material is then similar to the activated diffusion in zeolites.

In the case of zeolitic systems, it was found that the self-diffusion coefficients obtained by QENS and PFG NMR methods were in good agreement with those calculated from molecular dynamics (MD) simulations (Jobic et al., 1993). However in the case of amorphous materials, such as the silica used in this experiment, it is so far not possible to apply MD methods. Therefore one has to rely only on experimental techniques!

Acknowledgments

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