Quasi-elastic neutron scattering study of the mobility of methane in microporous silica

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Abstract

The dynamics of translation and rotation of methane in microporous bulk silica have been studied with quasi-elastic neutron scattering. At \( T = 200 \) K the self-diffusion coefficient of translation is \( D_T = 1.1 \times 10^{-8} \text{ m}^2 \text{s}^{-1} \) with an estimated activation energy of 4 kJ mol \(^{-1}\). Any variation of \( D_T \) with occupancy is within the experimental error of 50%. The isotropic rotational diffusion constant \( D_R \) is of the order of \( 10^{11} \text{ s}^{-1} \), with an experimental error of a factor of 2. The pore-size distribution has been studied with small angle X-ray scattering. A broad pore-size distribution is observed, with pores smaller than 10 Å. The largest fraction of pores is observed at the lower experimental limit, corresponding to a pore size of 2 Å. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Improvements in the synthesis of supported silica membranes have resulted in very thin defect free membrane layers [1]. Since these membranes have extremely small pores, comparable to those in Linde Type A zeolites [2], they show very low fluxes for molecules larger than methane, combined with large fluxes for smaller molecules. Given that their thermal and chemical stabilities by far exceed those of organic membranes, silica membranes can be considered good candidates for the removal of small gas molecules from gas mixtures containing hydrocarbons. Examples are found in the dehydrogenation of hydrocarbons and coal gasification [3,4].

Obviously, the mobility of methane in the microporous silica material is a crucial parameter for a proper understanding of the separation behaviour of silica membranes. This mobility may be studied by macroscopic techniques, such as chromatographic techniques, permeance and uptake measurements [5]. Such techniques yield a non-equilibrium chemical or transport diffusion coefficient \( D \), which is the parameter of proportionality between the diffusion flux and a gradient in composition. This parameter is generally not related to the mobility in a simple way [6]. Furthermore, in the interpretation of the macroscopic measurements...
one should account for problems such as heat transfer, surface barriers and percolation effects.

It would clearly be desirable to measure the mobility of methane on a microscopic scale. There are only two experimental techniques that can be used for this: pulsed field gradient NMR and quasi-elastic neutron scattering (QENS). Both techniques have been used to study the mobility of methane in zeolites, such as ZSM-5 [7,8] or NaY [9]. The reported data appear to be in good agreement with each other [10]. In this work, the mobility of methane in silica is studied with QENS. A strong correlation can be expected between the mobility of CH₄ and the pore-size distribution of the silica material. In the present work the pore-size distribution in the microporous silica is studied with small angle X-ray scattering (SAXS).

1.1. Theory

Neutrons are electrically neutral particles with a mass \( m_0 \), which may also be considered as plane waves with a wave vector \( \mathbf{k} \) of magnitude \( 2\pi/\lambda \). The wavelength of a neutron is related to its speed, and by changing the speed one can vary its momentum \( \mathbf{p} = \hbar \mathbf{k} \) and its energy \( E = \hbar^2 \mathbf{k}^2/(2m_0) \). The two parameters of interest in a neutron scattering experiment are the energy transfer \( \hbar \omega \) and momentum transfer \( \hbar \mathbf{Q} \) [11].

Experimentally one measures the double-differential cross section, i.e., the number of neutrons scattered in the angle \( d\Omega \), with energy in the range \( dE \). This cross section can be split up into contributions of incoherent and coherent scattering functions \( S(Q,\omega) \), which are the Fourier transforms of Van Hove [12] correlation functions \( G(r,t) \). These correlation functions describe the motions of the scattering species in space \( r \) and time \( t \).

Since the incoherent cross section of the hydrogen atom is very large (80 barns, 1 barn = \( 10^{-28} \) m\(^2\)) it is mainly the incoherent scattering function \( S_{\text{inc}}(Q,\omega) \) that contributes, and consequently individual motions are considered. The relevant motions include vibration, rotation and translation. These are assumed independent of each other, since they occur on different time scales. The total scattering function can be considered the convolution of the individual scattering functions, corresponding to the individual motions [13].

Rather than calculating the Van Hove (self) correlation function from the experimental data, a model is assumed for the motions and is fitted to the data. An extensive review on different models was presented by Jobic [14]. We found that the broadening of the elastic peaks could be described well by using the jump diffusion model proposed by Singwi and Sjölander [15] for translation (the SS model) and an isotropic rotational diffusion model for the rotation.

1.2. Rotation

Methane molecules may be considered to undergo rotations over small angles. Consequently, after time averaging they have no preferred orientation in space. For such rotating molecules the incoherent scattering law is given by [16]

\[
S(Q,\omega) = A_0(Q)\delta(\omega) + \frac{1}{\pi} \sum_{m=1}^{\infty} A_m(Q) \times \frac{m(m+1)D_R}{[m(m+1)D_R^2 + \omega^2]}
\]

(1)

where \( D_R \) is the isotropic rotational diffusion coefficient. The intensity of the elastic peak, \( \delta(\omega) \), is governed by the elastic incoherent structure factor (EISF) \( A_0(Q) \). The EISF and quasi-elastic structure factors are defined as

\[
A_m(Q) = (2m+1)j_m^2(QR)
\]

(2)

where \( R \) is the radius of gyration (\( R = 1.1 \) Å for methane) and \( j_m(x) \) is the spherical Bessel function of order \( m \). For the \( Q \) range covered here, the main quasi-elastic contribution is that corresponding with \( m = 1 \).

1.3. Translation

In the SS model, the normalised jump length distribution is of the form \( \rho(r) = r/r_0^2 \exp(-r/r_0) \), so that the mean-square jump length is
\[ \langle r^2 \rangle = \int_0^\infty r^2 \rho(r)dr = 6r_0^2 \]  

In the simplified version of the SS model, the average time taken for a jump of a molecule is much shorter than the residence time on its site, \( \tau \). For an isotropic system, the scattering function is a Lorentzian with a half width at half maximum (HWHM) corresponding to

\[ \Delta \omega(Q) = \frac{1}{6\tau} \frac{Q^2 \langle r^2 \rangle}{1 + Q^2 \langle r^2 \rangle / 6} \]  

For small \( Q \), the right hand side of Eq. (4) reduces to \( Q^2 \langle r^2 \rangle / 6\tau \). Using Einstein’s expression in three dimensions

\[ D_S = \langle r^2 \rangle / 6\tau \]  

with \( D_S \) the self-diffusion coefficient of translation, this is equal to \( D_S Q^2 \). Consequently, at low \( Q \) the width of the Lorentzian should vary linearly with \( Q^2 \).

2. Experimental

2.1. Quasi-elastic neutron scattering

The preparation of the silica sample is described elsewhere [17]. For the neutron measurements, the sample was dehydrated by heating it to 573 K in vacuum. After cooling, the flakes were transferred into a circular aluminium cell (wall thickness 1 mm, \( \Omega = 50 \) mm). In order to get enough scattering from the adsorbate, a large quantity of silica sample was used, i.e., 18 g.

The neutron scattering experiments were performed on the time of flight (TOF) spectrometer IN5 at the Institut Laue–Langevin, Grenoble. The wavelength of the incident beam was 9 Å. The cell was placed under an angle of 135° and energy spectra were recorded at 88 different angles in the range 13° < 2θ < 126°. Grouping of different angles was performed to obtain sufficiently good statistics. A vanadium run was performed to obtain the energy resolution and the detector efficiencies. The resolution function of the spectrometer could be fitted with a Gaussian function, the full width at half maximum varying from 17 µeV at low \( Q \) to 21 µeV at high \( Q \). Runs for the silica material in vacuum were performed at 100, 200 and 300 K. The temperature was controlled by a liquid N\(_2\) cooling loop combined with an electric heating element. Three different occupancies of methane were measured at 200 K and two at 250 K. Assuming Langmuir type sorption behaviour, the occupancies \( (q/q_{\text{sat}} \) with \( q \) the sorbed concentration and \( q_{\text{sat}} \) its saturation value) were determined in situ from a volumetric analysis.

2.2. Small angle X-ray scattering

The measurements were performed on a home-made apparatus [18]. The silica powder was out-gassed in situ by flushing the cell with helium, while slowly heating up the sample to 573 K. The SAXS data were analysed with the multiple scattering theory [18]. Size distributions of heterogeneities were calculated from a Patterson function obtained by Fourier transformation of the data. The scattering elements were assumed to have a spherical shape. A discrete distribution function \( F_r \) was derived that describes the fractions of sample volume within a certain size interval.

3. Results and discussion

The relatively high concentration of silanol groups in the sample (\( \approx 7.5 \times 10^{20} \) g\(^{-1}\), estimated from comparison with the elastic spectra of a silicalite sample for which the number of silanol groups was determined independently) produces a strong elastic signal and results in a large temperature dependence. Consequently, a proper correction for the bare sample (i.e., the silanol groups) is crucial in the analysis of any data. In Fig. 1 the amorphous nature of the silica can clearly be recognised. This figure depicts the neutron diffraction pattern of silica at \( T = 100 \) K, which was obtained by comparing the intensities of the elastic peaks at each angular position with those measured with a standard vanadium plate. There are no Bragg peaks present in the spectrum, and at low \( Q \) there is a distinct contribution of small angle scattering (SAS).
The $Q$ range covered by the TOF spectrometer was not sufficient to interpret the SAS data in terms of morphology of the silica material. For this purpose SAXS measurements were performed. Fig. 2 depicts the resulting pore-size distribution. From the figure it appears that the pores are smaller than 10 Å. The largest fraction of pores is observed at the lower experimental limit, corresponding to a pore size of 2 Å.

Fig. 3 shows a comparison between experimental and calculated QENS spectra, for an occupancy of 29%, at 200 K. After corrections for the incident neutron flux, detector efficiency, absorption and self-shielding, the contribution from the bare silica was subtracted. For the spectra at low $Q$ this subtraction procedure resulted in a negative elastic peak, which may be attributed to the influence of sorbed methane on SAS. At high values of $Q$ also a negative peak is observed. The contribution of SAS in this $Q$ range will also have changed, but the negative peak is in this case more likely due to an over-correction for the bare silica.

In the fitting procedure an extra parameter was used to account for the occurrence of a negative or positive additional elastic intensity. Since the broadening due to translation and rotation is large with respect to instrumental resolution (see Fig. 4), the extra parameter has a negligible influence on the values obtained for $D_S$ and $D_R$.

In Table 1 the neutron transmission is given for different degrees of occupancy. In case of low transmission values (e.g. 0.81) some multiple scattering will occur [13]. The error introduced due to multiple scattering is here simply included in the total experimental error.

3.1. Rotation

For small values of $Q$ the quasi-elastic contributions of rotation are negligible, while they become more eminent at increasing $Q$. In the $Q$ range covered here the term in Eq. (1) that has the largest contribution is that for which $m = 1$. The HWHM
of the broadening due to rotation is consequently 2 \( D_R \).

Fig. 4 shows the contribution of rotation to broadening at \( Q = 0.977 \text{ Å}^{-1} \). Under the conditions employed here \( D_R \) is approximately \( 10^{11} \text{ s}^{-1} \) and any variation of \( D_R \) with occupancy or temperature remains within experimental error, which is a factor of 2. The value of \( D_R \) is slightly larger than that in ZSM-5, but it is still small compared to that of methane adsorbed on graphite or in bulk solid methane [8]. This indicates that interactions of methane with the silica network are present.

### 3.2. Translation

The broadening as function of \( Q^2 \) is plotted in Fig. 5 for an occupancy of 29% at \( T = 200 \text{ K} \). For small \( Q \) the self-diffusion coefficient can be obtained from the linear relation between the broadening and \( Q^2 \). The values obtained can be found in Table 1. The experimental error is of the order of 50%, and any variation of the self-diffusion coefficient with occupancy is within this error. The relatively large value of the experimental error is due to the high concentration of silanol groups. Without silanol groups present in the sample, the error would have been \(~20\%\).

All the spectra could be fitted simultaneously with the SS model. The average jump lengths \( \langle r^2 \rangle^{1/2} \) are about 8 Å at 200 K and 9 Å at 250 K. The jump diffusion model reaches normal diffusion (Eq. (5)) at small \( Q \) values (linear regime), corresponding to distances of about 30 Å. There is a small variation of \( D_S \) with temperature; an estimation of the activation energy \( E_a \) based on the two temperatures gives a value of 4 kJ mol\(^{-1}\), which is similar to that in ZSM-5 [8] and smaller than that in zeolite NaY (6.3 kJ mol\(^{-1}\) [9]).

The mobility of methane in silica is about five times larger than in ZSM-5, 2.5–3.7 \( \times \) 10\(^{-9} \) m\(^2\) s\(^{-1}\) at 200 K, 4.5–6.3 \( \times \) 10\(^{-9} \) m\(^2\) s\(^{-1}\) at 250 K, depending on the loading [8]. It is two times larger than in NaY or NaX [9]. This would indicate that the pores which methane is able to access are in the range 4–8 Å, which is in fair agreement with the pore-size distribution obtained from the SAXS measurements performed here and nitrogen sorption measurements performed by De Lange et al.
Similar observations were made for H₂ in silica [20]. This pore size is small compared to that of a microporous silica material studied earlier by SAXS and QENS (~1 nm [21]).

Supported thin silica membranes show almost no permeance for methane (with a kinetic diameter of 3.8 Å) and larger molecules. This suggests that the pores in the supported thin layers are smaller than those in the unsupported material, which is consistent with the observations of a spectroscopic ellipsometry study of the sorption properties of a supported thin silica layer [22].

4. Conclusions

Using QENS the translational and rotational dynamics of methane in unsupported microporous silica have been studied. Despite the high concentration of silanol groups in the material, both the self-diffusion coefficient $D_S$ and isotropic rotational diffusion constant $D_R$ have been measured as function of temperature and degree of occupancy.

At $T = 200$ K the values of $D_S$ and $D_R$ are $1.1 \times 10^{-8}$ m² s⁻¹ and $10^{11}$ s⁻¹, respectively. Variation of $D_S$ and $D_R$ with occupancy is within experimental error (50% and a factor of 2, respectively). A crude estimation of the activation energy $E_m$ of $D_S$ yields a value of 4 kJ mol⁻¹, which is similar to the value found for methane in ZSM-5.

SAXS measurements have been performed to study the morphology of the sample. The data obtained indicate a relatively broad pore size distribution with almost all pore sizes below 10 Å. The largest fraction of pores is observed at the lower experimental limit, around 2 Å. Such a pore size distribution is in fair agreement with the results of the QENS measurements and with results reported in literature, obtained by using nitrogen physisorption. The pore size in the bulk material is larger than that in supported thin silica membranes, which was also observed in a spectroscopic ellipsometry study of the properties of thin supported silica membranes.

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References