

Methane dynamics in porous xerogels characterized by small-angle and quasielastic neutron scattering

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Abstract

The melting behavior of methane adsorbed in a porous silica xerogel has been examined by quasielastic neutron scattering (QENS) from 20 to 115 K. The methane dynamics indicate a heterogeneous xerogel surface with a distribution of rotational and translational diffusion barrier heights from 0.17 to 2.1 kJ/mole. The QENS elastic intensity structure factor indicates that rotational diffusion occurs about a C₂ molecular axis for methane adsorbed in the xerogel. Porous silica and aluminosilica xerogels have also been characterized by small-angle neutron scattering (SANS) and gas adsorption isotherm measurements to determine the porosity, pore size, and tortuosity of the pore network. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Porous silica or metal oxide glasses obtained by sol-gel polymerization have been investigated as host materials for a variety of diverse applications including chemical sensing, drug delivery, lasing media, and catalysis [1]. The current study aims to provide a physical understanding of the structure of the porous matrix and the effect that the xerogel matrix has on

the dynamics of molecules (e.g. methane) entrapped within the porous network of the matrix.

Sol-gel glasses are typically formed by the hydrolysis (1) $\text{M-OR} + \text{H}_2\text{O} \rightarrow \text{M-OH} + \text{HOR}$, and subsequent polycondensation (2) $\text{M-OH} + \text{HO-M} \rightarrow \text{M-O-M} + \text{H}_2\text{O}$ of a metal alkoxide precursor. Aging and drying of the subsequent gel can lead to a dry porous xerogel glass with a large net porosity. The control of pore volume, pore surface area, and pore size distribution by chemical means has been well demonstrated [2–6]. Xerogel pore diameters can vary from roughly 10 to 100 Å depending on the chemical protocol used in preparation. Pore volume can be greater than 90% if aerogel processing is used [1]. The ability to control these properties of the matrix makes sol-gel based materials promising for a wide range of applications. For

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chemical sensing applications, the porosity, surface area, and pore size are critical parameters which affect sensitivity, selectivity, and sensor lifetime [7]. The structural characteristics of the sol-gel matrix are typically controlled by varying the pH and the water to alkoxide precursor ratio to yield desired structural properties of the resulting xerogel.

The effect of synthesis pH on the resulting structure of xerogels is well documented [8,9]. Low pH favors the hydrolysis reaction, leading to dense structures with low porosity and small pore size distributions. While sol-gel mixtures with more neutral pH favors the condensation reaction, leading to more highly branched structures with higher porosity and larger pore size distributions [8].

Small-angle neutron scattering (SANS) is useful for the study of structures in the size range of 10 to 100 Å. SANS has been used to characterize the structural evolution of porous titania–silica and zirconia–silica gels [10,11], the structural changes induced by organic modification of silica xerogels [12], as well as the structure of porous vycor glass [13]. Small-angle x-ray scattering has also revealed the fractal geometry for extremely low density silica aerogels [14]. In the present study SANS data has been obtained for three different silica xerogels and one aluminosilica xerogel. Analysis of the SANS data yields details of the spatial density variations in the material, such as the mean size, shape, and the distribution of pore sizes [15] within the xerogel matrix.

Quasielastic neutron scattering (QENS) can be used to study rotational and translational dynamics of hydrogenous materials [16–21]. In the present study, QENS is used to study the translational and rotational behavior of methane adsorbed to the surface of a silica xerogel. Temperature dependent QENS reveals a heterogeneous distribution of activation energies for translational diffusion. Further anal-

ysis of the momentum transfer dependence of the elastic intensity structure factor indicates that rotational diffusion about a C₂ molecular axis occurs below the melting temperature of methane within the porous xerogel matrix.

2. Experimental

2.1. Preparation of xerogel glasses

Silica sol–gel glasses were prepared by mixing 0.01N hydrochloric acid, tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS) (from Gelest, Inc.), and ethanol, in the proportions listed in Table 1. Three silica samples (SX2, SX4, SX6) were prepared under different pH conditions. The SX2 sample was polymerized at a pH ~ 2, the SX4 sample was allowed to undergo acid-catalyzed hydrolysis at pH ~ 4 for 12 h before the addition of ammonium hydroxide, whereas for the SX6 sample a potassium phosphate solution (pH 6.8, 50 mM) was used to fix the pH.

Aluminosilica xerogels (ASX) were prepared by mixing di-s-isobutoxyaluminotriethoxysilane (AIOS) (Gelest, Inc.), isopropanol, and water in a 0.08:0.5:1.0 ratio, as listed in Table 1. The solutions were sonicated, poured into sealed polystyrene molds, allowed to slowly gel and dry (two weeks). For the present study samples were produced with dimensions ~ 2 mm × 5 mm × 10 mm.

2.2. Small-angle neutron scattering

The small-angle neutron scattering measurements were carried out with the time-of-flight small angle diffractometer [22] at the Intense Pulsed Neutron Source (IPNS, Argonne National Laboratory). This instrument uses neutrons produced in pulses by spal-

Table 1
Xerogel recipes

Name	Method	Alkoxide	Molar ratios (H ₂ O : Alcohol : Alkoxide : HCl)
SX2	acid catalyzed	TEOS	1.0 : 3.0 : 0.3 : 2×10^{-4}
SX4	2 step (acid/base)	TEOS	1.0 : 2.0 : 0.2 : 1.2×10^{-4}
SX6	Neutral buffered	TMOS	1.0 : 0 : 0.05 : 5×10^{-6}
ASX	Aluminosilica	AIOS	1.0 : 0.5 : 0.08 : 0.0

lation due to the collision of 450 MeV protons with a depleted uranium target. A solid methane moderator (22 K) is used to obtain neutron wavelengths in the range 0.5 to 14 Å. The scattered neutrons were detected with a 20 cm × 20 cm gas-filled proportional counter array. The SANS instrument can provide useful data in the momentum transfer (Q) range from 0.007 to 0.25 Å⁻¹ ($Q = \frac{4\pi}{\lambda} \sin \theta$, where θ is half the scattering angle, and λ is the wavelength of the incident neutrons). The reduced data were transformed to an absolute scale by a routine IPNS procedure, yielding absolute differential scattering cross sections.

Samples used with SANS were heated to 150°C at 10⁻⁵ Torr for 12 h prior to measurements. SANS measurements were made at 50°C under a flow of nitrogen gas to reduce the condensation of water within the pores of the xerogels. Four different xerogel samples (SX2, SX4, SX6, ASX) were studied with SANS. As listed in Table 1, SX2 and SX4 were produced using tetraethoxysilane (TEOS) as the sol-gel precursor, whereas SX6 was prepared using a low alcohol and high water content ratio with tetramethoxysilane (TMOS) as the sol-gel precursor. This SX6 protocol is commonly used in the doping of proteins into xerogels [23].

2.3. Quasielastic neutron scattering

Xerogel samples with a collective mass of 0.75 g were used for QENS measurements. The SX4 monoliths were formed by acid-catalyzed hydrolysis followed by base-promoted condensation. The total molar ratio of tetraethoxysilane:ethanol:water:hydrochloric acid:ammonium hydroxide was 0.2:2:1:1.2 × 10⁻⁴:3 × 10⁻³, as listed in Table 1. After 12 h of hydrolysis in hydrochloric acid aqueous ammonium hydroxide was added to promote condensation. The mixture was poured into polystyrene cuvettes and allowed to gel, age, and dry over two months. Prior to QENS measurements the monoliths were heated to 250°C at 10⁻⁵ Torr for 6 h to remove water and alcohol from the sample pores. The quasielastic scattering experiments were carried out on the QENS spectrometer at IPNS (Argonne National Laboratory) [24]. The elastic resolution was 90 μeV, and twelve spectra were obtained in the

Q -range 0.5 to 2.5 Å⁻¹. The sample was dosed in-situ, in a cylindrical sample container, 5 mm internal diameter by 100 mm long. No corrections were made for multiple scattering. 25 Torr-L of methane was taken up by the sample. This corresponds to roughly 90% of a monolayer based on a BET surface area of 500 m²/g [25]. QENS measurements were made for a temperature range of 20 to 115 K. The QENS intensity was fit with the sum of a delta function plus a Lorentzian band.

2.4. Nitrogen adsorption isotherms

Nitrogen adsorption isotherms were performed at 77 K. Brunauer–Emmett–Thomas (BET) analysis was used to determine the specific surface areas of the samples [25]. Total pore volume was calculated from the volume of adsorbed nitrogen at 0.95 P_0 . Desorption isotherm measurements were performed on two of the samples, but variability in these measurements precluded reliable determination of pore size by isotherm analysis [26].

3. Results and discussion

3.1. Small-angle neutron scattering

The mean xerogel pore size can be determined from the SANS data. Pore size information is obtained by analyzing the scattering intensity $I(Q)$ in the low Q regime ($R_g \cdot Q \leq 1$) using the Guinier approximation [15],

$$I(Q) = I(0) \exp(-Q^2 R_g^2 / 3), \quad (1)$$

where the radius of gyration R_g is the root-mean-squared distance of all the atoms from the centroid of the neutron scattering length density distribution of the particle. $I(0)$ is the scattering intensity at zero momentum transfer (Q) given by

$$I(0) = N_s (\rho_m - \rho_p)^2 V^2, \quad (2)$$

where N_s and V are the number density and the volume of the scatterers (pore) respectively. The contrast, $\rho_m - \rho_p$, is the difference in the scattering length densities of the glass matrix and the pores, respectively.

The silica xerogel formed at pH 2 (SX2) shows very little scattering over the measured Q region. Measurements of thin samples (0.05 cm) as well as thick samples (0.5 cm) failed to produce a significant scattering signal. This lack of scattering is indicative of a material with low pore volume and/or a small pore size distribution. This is consistent with our inability to measure a BET surface area for this sample with nitrogen adsorption measurements at 77 K. Microporous structures have been associated with acid-catalyzed silica xerogels [27]. Hence we

present the data only for the SX4, SX6 and ASX samples.

Guinier plots of the SANS data from SX4, SX6 and ASX are shown in Fig. 1a. From a plot of $\ln[I(Q)]$ versus Q^2 , a linear fit is made in the region where $Q \cdot R_g$ is between 0.8 and 1.1. The R_g and $I(0)$ values can be obtained from the slope and the y-intercept of the linear fit, respectively.

If the pores have a rod-like morphology the SANS data for the xerogels can also be used to determine their cross-sectional radii by use of modified Guinier

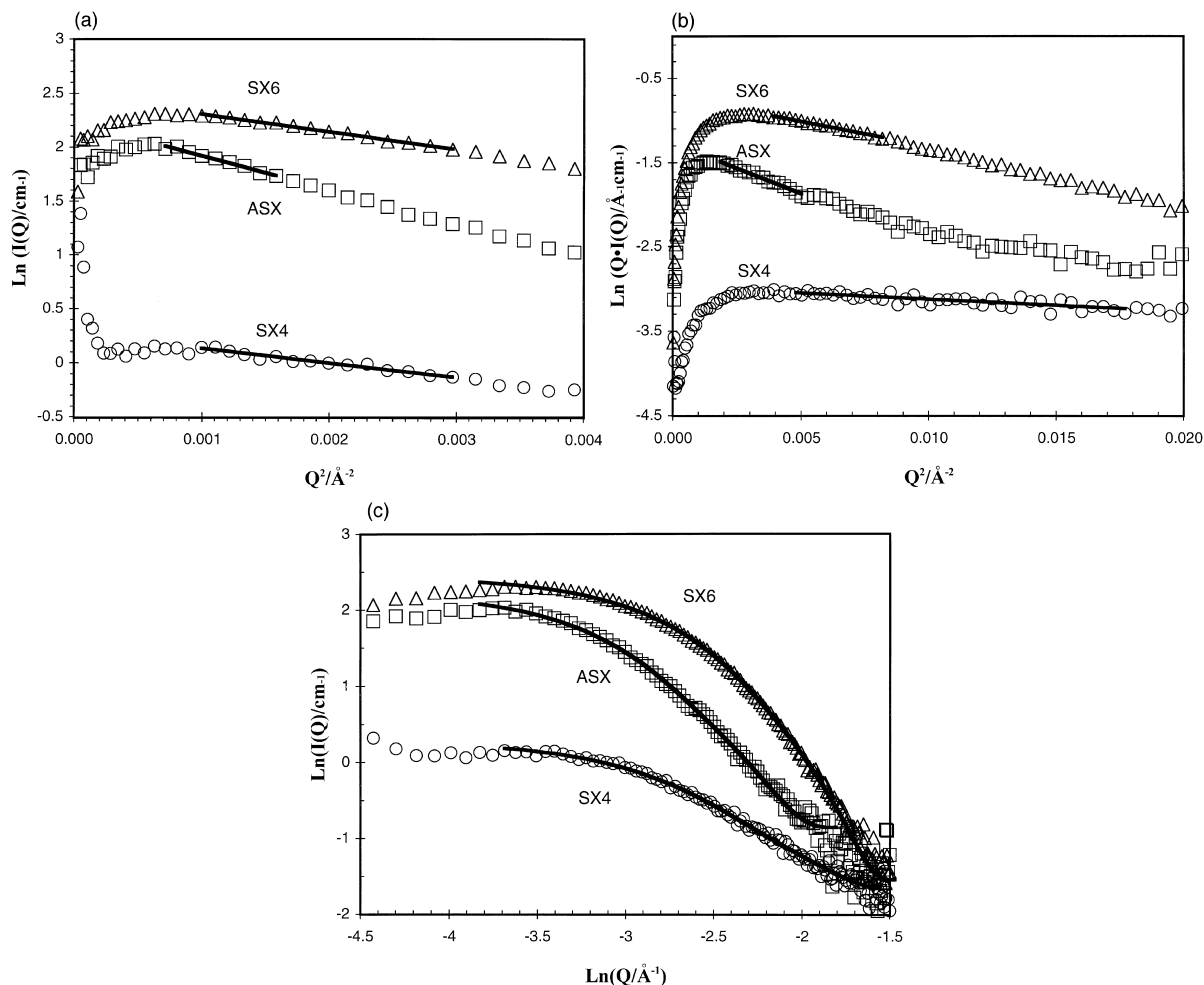


Fig. 1. (a) The logarithm of the SANS intensity $I(Q)$ versus the square of the momentum transfer Q^2 for SX4, SX6, and ASX xerogels. The solid line is a Guinier fit to Eq. (1), yielding the radius of gyration R_g listed in Table 3. (b) The logarithm of $Q \cdot I(Q)$ versus the square of the momentum transfer Q^2 for SX4, SX6, and ASX xerogels. The solid line is a modified Guinier fit to Eq. (3) assuming cylindrically shaped pores. The average cross-sectional radii values are listed in Table 3. (c) A log-log plot of the SANS intensity versus momentum transfer. The solid curves are fits to Eq. (4) using a form factor for a circular cylinder. The average radius and the length of the pores for each xerogel are listed in Table 3.

analysis [28]. In this type of analysis, the scattered intensity in the low Q region is approximated by the equation

$$I(Q) = \frac{1}{Q} I_C(0) \exp(-Q^2 R_C^2 / 2), \quad (3)$$

where R_C is the cross sectional radius of gyration and the radius, $R = \sqrt{2} R_C$. Fig. 1b shows the modified Guinier plots $\ln[QI(Q)]$ versus Q^2 of the SANS data for SX4, SX6 and ASX. The existence of a linear region where $Q_{\max} R_C < 1$ is evidence that the pores are cylindrical in shape. R_C can be determined from the absolute value of the slope by, $R_C^2 = 2 \cdot (\text{slope})$. The bend over in the low Q^2 region for all the glasses implies that the pores are limited in length. Furthermore, this feature in the SANS data occurs at much lower Q^2 for the ASX samples than for SX4 and SX6, implying that the pores in ASX are longer than in the other xerogels. The radii values from the modified Guinier analysis are given in Table 3.

Since the modified Guinier analysis gave evidence that the pores are rod-like we fit the SANS data for all the glasses to the scattering form factor for a circular cylinder of length L and radius R [15],

$$I(Q) = I_0 \int_0^{\pi/2} \frac{2 J_1(QR \sin \alpha)}{QR \sin \alpha} \frac{\sin((QL \cos \alpha)/2)^2}{(QL \cos \alpha)/2} \times \sin \alpha d\alpha, \quad (4)$$

where J_1 is the first order Bessel function. Fig. 1c shows the SANS data for the three xerogels including best fits to Eq. (4). The two silica xerogels formed at higher pH as well as the aluminosilica sample show a broad scattering peak near $Q_{\text{peak}} = 0.03 \text{ \AA}^{-1}$ (Fig. 1c). This broad peak in the data is attributed to pore–pore correlations in which cylindrical pores are organized with an average distance between the pore centers of about $209 \text{ \AA}$ ($2\pi/Q_{\text{peak}}$). As can be seen from Fig. 1c we obtain reasonable fits of Eq. (4) to the SANS data from high Q down to Q values near the broad peak. The fits to Eq. (4) yield radii and lengths of the pores which are listed in Table 3.

To further assess the validity of the size parameters obtained for the pores we compared the R_g values obtained by fitting the SANS scattering to the cylinder form factor (wide Q region, Eq. (4)) versus

R_g values obtained from Guinier analysis (low Q region, Eq. (1)). The radius of gyration for a cylinder is related to the radius R and the length L by

$$R_g^2 = R^2/2 + L^2/12. \quad (5)$$

The R_g values obtained by inserting into Eq. (5) the pore radii and length values obtained from the cylinder fits for SX4, SX6 and ASX, yield 22.4, 22.5 and $32.7 \text{ \AA}$, respectively, as listed in Table 3. These values agree well with the R_g values determined from the Guinier analysis, which are also listed in Table 3 for comparison. The consistency between the parameters derived from different kinds of analysis confirms that the morphology of pores in these samples is cylindrical.

The pore radii values for SX6 and ASX obtained by fitting the SANS data to the Eq. (4) agree with those from the modified Guinier analysis given by Eq. (3). However, there is a discrepancy between the R and L values obtained using Eq. (3) versus Eq. (4) for SX4. It is important to note that the radius obtained from the modified Guinier analysis (Eq. (3)) is derived from the low Q region, while the radius from the cylinder fit (Eq. (4)) comes from the high Q region. The discrepancy between these radii values for SX4 suggests that while the majority of the SX4 pores may be small, there exists a smaller population of larger pores which only contribute to the values obtained by the cylindrical form factor fits.

From Eq. (2) the intensity of the QENS intensity is strongly dependent on the number and the volume of the scatterers, in this case the pores of the xerogels. For the silica xerogels the highest intensity is observed for the sample formed near pH 6 (SX6). The scattering intensity from the silica xerogel formed near pH 4 (SX4) is weaker but there is still a visible peak. Given our knowledge of the pore dimensions, the xerogels can be ranked in order of total pore volume from the intensity of the scattering curves. The SX6 sample possesses the highest porosity followed by the aluminosilica xerogel. The SX4 sample is even less porous with the SX2 sample possessing a significantly lower pore volume. This ordering is confirmed by nitrogen adsorption measurements discussed in the next section.

The consistency of the sol-gel pore structure was tested by comparing measurements from different

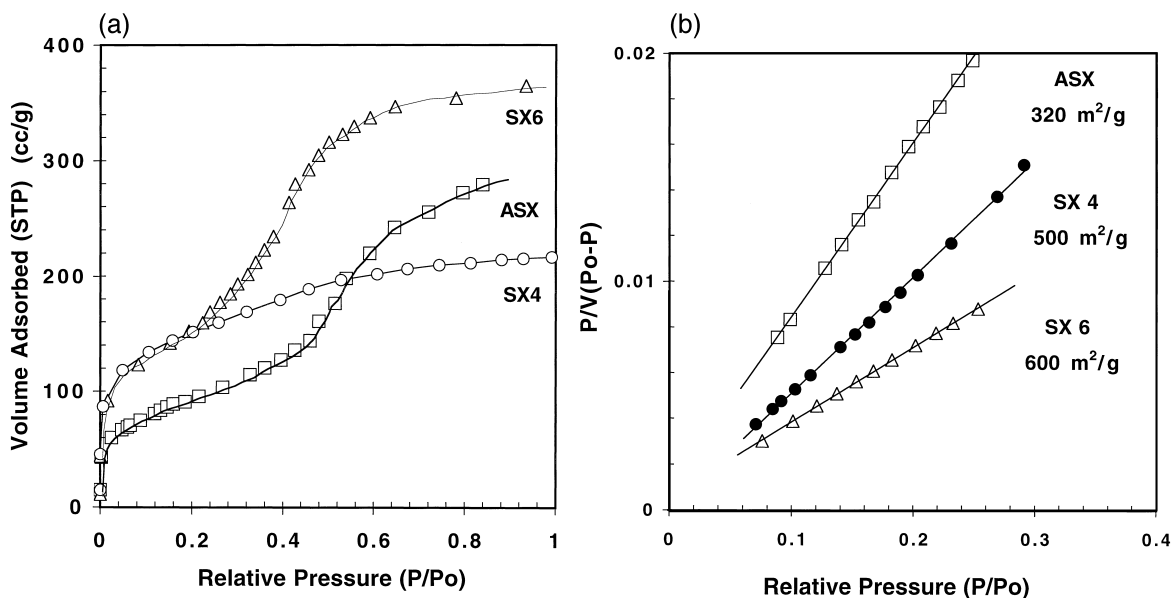


Fig. 2. (a) Nitrogen adsorption isotherms for SX4, SX6, and ASX xerogels, made at 77 K. (b) BET plots of the data yield the surface areas of the different porous xerogel glasses, which are listed in Table 2.

samples produced by the SX4 protocol. Scattering from two thick samples (0.5 cm) and two thin samples (0.05 cm) was measured. Three of the four measurements resulted in consistent data, however, scattering from one of the thin samples did not show the characteristic broad peak near $0.03 \text{ \AA}^{-1}$. The variability in this film is attributed to the volatility of ammonia which can affect the concentration of ammonium hydroxide used to raise the pH and promote condensation in the SX4 samples.

3.2. Nitrogen adsorption isotherms

The volume of xerogel pores can also be measured with gas adsorption isotherms [24]. Fig. 2a shows nitrogen adsorption isotherms and Fig. 2b shows BET plots performed at 77 K. The SX6 and ASX isotherms show significant capillary condensation, indicating that both materials are mesoporous substances. The isotherm for the SX4 sample does not show this capillary condensation, indicative of a microporous material. The SX2 sample did not adsorb significant amounts of nitrogen at 77 K. This behavior has previously been observed for acid catalyzed silica xerogels [27]. The lack of adsorption for

this sample is consistent with the existence of small pores with a high activation energy for adsorbates to enter the pores of the glass. The isotherm pore volumes and surface areas are given in Table 2. The isotherm pore volumes are consistent with the small-angle neutron scattering data. The SX6 sample has the highest porosity followed by the ASX and SX4 samples. Although the SX2 sample did not adsorb nitrogen or show appreciable neutron scattering it is a porous material. Water immersion measurements show the porosity of SX2 to be about 20%. Immersion experiments show that SX4 samples have porosities of about 30%, and ASX and SX6 samples possess about 55% pore volume.

The mean pore size can be estimated by adsorption isotherm data and compared with the results

Table 2
Adsorption isotherm pore volumes and BET surface areas

Sample	Pore volume (cm ³ /g)	BET surface area (m ² /g)
SX 4	0.20	500
SX 6	0.36	600
ASX	0.29	320

obtained by SANS. For cylindrical pores the mean pore radius, $r_p = 2V/A$, where V is the total volume of condensed gas in pores of the sample and A is the total internal surface area. The cylindrical pore radius values obtained from adsorption isotherm measurements are compared with the SANS results in Table 3. The results in Table 3 show that the pores are tortuous in SX4, SX6, and ASX (i.e. length = 1.5 to 2.5 times diameter). Eq. (2) also indicates that the SANS scattering intensity is proportional to the product of the number of scatterers and the square of the volume of the scatterer. Although the average pore size in SX6 is smaller than for ASX (Table 3), the absolute scattering intensity for SX6 is observed to be larger than for ASX (Fig. 1). This indicates that the increased scattering of the SX6 xerogels is due to a larger number of pores in SX6, which is consistent with the higher total pore volume measured for SX6 by nitrogen condensation measurements, listed in Table 2.

High acidity in the processing of the sol leads to a polymerization process in which gel particles pack together well, leading to a xerogel structure with small pores. When the pH of the sol is increased, more branching occurs during the polymerization process, leading to less dense packing of the gel particles and larger pores. The chemistry of the aluminosilica xerogel is more complex since both silicon alkoxides and aluminum alkoxides are hydrolyzed during the process of polymerization. Due to its lower electronegativity, the aluminum alkoxide groups are more easily hydrolyzed than the silicon alkoxide groups [29]. This fact is evident in the observation that no acid catalyst is required for the

production of the aluminosilica xerogel. The material gels within several minutes without the use of a catalyst. The absence of acid catalyst yields a solution with higher pH than for acid-catalyzed gels. Consequently, the pores in the resulting xerogel are large compared to their acid-catalyzed silica counterparts.

3.3. Quasielastic neutron scattering

The QENS intensity data was fit by the sum of a delta function (elastic peak) plus a Lorentzian band (inelastic). The elastic contribution contains information on the geometry of the diffusive process. The elastic incoherent structure factor (EISF = elastic intensity/total intensity) is used to probe changes in the elastic intensity with as a function of momentum transfer (Q) or temperature.

Methane motion within the pores of the SX4 xerogel is evident by the drop of the elastic incoherent structure factor (EISF) with increasing temperature, as shown in Fig. 3a. The drop in the EISF is caused by the motion of the adsorbed methane on the surface of the xerogel pores. A sharp drop in the EISF is indicative of a cooperative phase change of the adsorbed material. However, the temperature dependent drop in the EISF shown in Fig. 3a is more gradual than what has been reported for the semi-crystalline porous silica MCM-41 [19]. The higher momentum transfer measurements ($Q = 1.79, 2.45 \text{ \AA}^{-1}$) show a gradual drop in the EISF from 35 to 105 K, while the low momentum transfer measurement ($Q = 1.02 \text{ \AA}^{-1}$) does show a drop in the EISF near the bulk melting temperature of 90 K.

Table 3

Summary of pore dimensions obtained from SANS and adsorption isotherm results. Guinier analysis (Eq. (1)), modified Guinier analysis (Eq. (3)), and cylindrical form fit results (Eq. (4)) of SANS data are compared with the cylindrical pore radius, r_p , obtained from adsorption isotherm measurements

Sample	Guinier analysis using Eq. (1)		Modified Guinier using Eq. (3) radius (Å)	Cylindrical form fit using Eq. (4)		R_g from Eq. (4) & Eq. (5) R_g (Å)	Isotherm data $r_p = 2V/A$ r_p (Å)
	R_g (Å)	$I(0) (\text{cm}^{-1})$		cylinder radius (Å)	cylinder length (Å)		
SX4	20 ± 0.5	1.3 ± 0.02	8 ± 0.4	16 ± 0.5	67 ± 1.5	22.4 ± 0.4	13
SX6	22 ± 0.5	11.9 ± 0.1	16 ± 0.5	17 ± 0.5	66 ± 1.0	22.5 ± 0.4	19
ASX	31 ± 0.8	9.3 ± 0.2	22 ± 0.5	21 ± 0.5	101 ± 1.0	32.7 ± 0.3	30

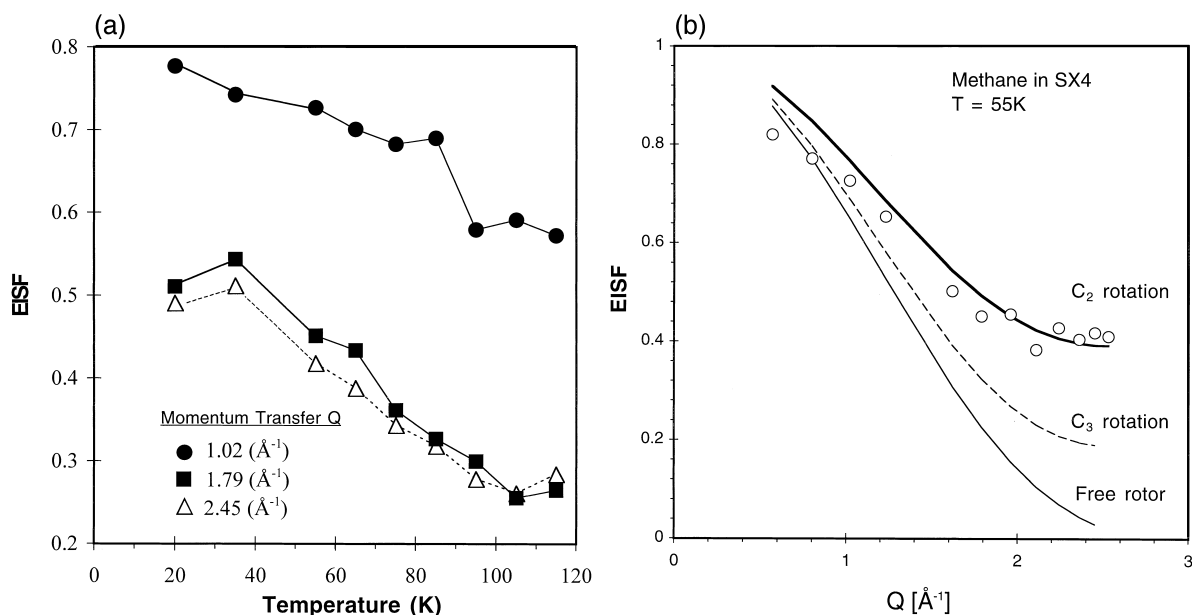


Fig. 3. (a) Elastic incoherent structure factor (EISF) for three momentum transfer values for methane adsorbed to a silica xerogel. The decrease in the elastic intensity with increasing temperature indicates the onset of dynamic phase transitions. Rotational melting may be responsible for the EISF decrease below 50 K whereas the EISF decrease from 65 to 90 K is indicative of translational melting. (b) Representative Q -dependent EISF data ($T = 55$ K) for a monolayer of methane adsorbed in SX4 below the translational melting temperature. The three fits correspond to rotation about a C_2 molecular axis (Eq. (6a)), rotation about a C_3 axis (Eq. (6a)), and free rotation on a sphere (Eq. (6b)). The best fit corresponds to rotation about a C_2 molecular axis.

These observations are consistent with the amorphous structure of xerogels giving rise to a broad distribution of adsorption sites. In contrast, the semi-crystalline MCM-41 material has a narrow distribution of surface adsorption sites and shows a sharper 'melting' transition for adsorbed methane [19].

Rotational and translational diffusion for methane in SX4 was analyzed using QENS linewidth measurements obtained versus temperatures and momentum transfer, as illustrated in Fig. 4a. The Lorentzian linewidth is effectively independent of Q from 20 to 65 K, indicating that the QENS linewidth is due to rotational diffusion at low temperature. In contrast, the Q -dependent broadening of the Lorentzian linewidth (proportional to Q^2 at low Q) at 115 K is indicative of translational diffusion. The 115 K temperature is well above the 90 K melting temperature for bulk methane, and the Q -dependent QENS results indicate that methane is able to diffuse along the surface of the xerogel pores [30]. The convolution of rotational and translational broadening and the energy resolution of the QENS spectrometer

makes determination of the translational diffusion constant imprecise. However, a jump translation plus rotation model fit to the 115 K data yielded a jump length of $l = 7.8$ Å and a residence time of $\tau = 19$ ps, corresponding to a translational diffusion constant of $D = l^2/6\tau \approx 5.3 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$. This value is somewhat larger than $D = 2.7 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ at the triple point of pure methane at 91 K [19].

The symmetry of the rotational motion of the methane adsorbates in SX4 can be obtained from a detailed analysis of the form of the Q -dependence of the EISF, as illustrated in Fig. 3b. Three models of the geometry of methane rotation were used to fit the Q -dependent EISF data, rotation about the molecular C_2 axis, rotation about the C_3 axis, and free rotation, as shown in Fig. 3b. The Q dependence of the EISF for rotation about m equidistant sites on a circle of radius r is given by [31]

$$\text{EISF}(Q) = m^{-1} \sum_{i=1}^m j_0(2Qr \sin(\pi i/m)), \quad (6a)$$

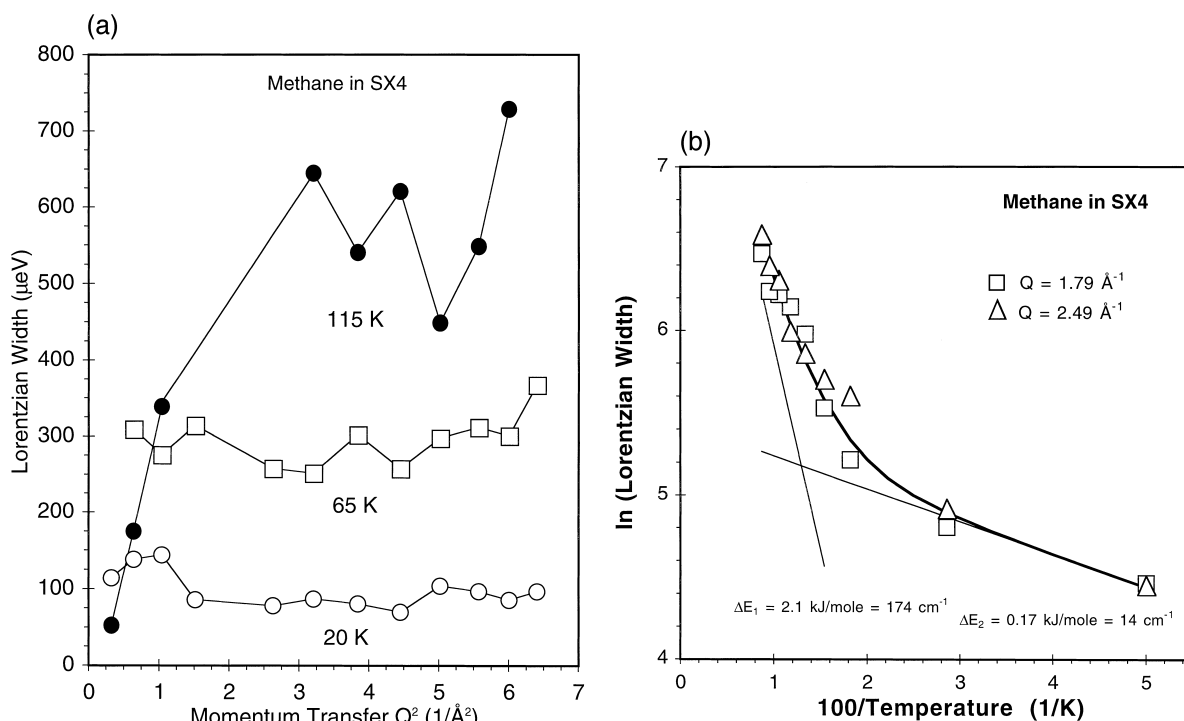


Fig. 4. (a) The Q -dependence of the QENS Lorentzian linewidth for a monolayer of methane adsorbed in a porous SX4 xerogel at three different temperatures. The Q -independent linewidth observed at 20 and 65 K is characteristic of rotational diffusion of methane. The Q -dependent linewidth at 115 K indicates translational diffusion. (b) An Arrhenius plot of the temperature dependence of the QENS Lorentzian linewidth. Data for three different Q values are plotted. The solid curve is a fit to a bimodal distribution of activation energies, with weighting of 95% $E_1 = 2.1$ kJ/mole, and 5% $E_2 = 0.17$ kJ/mole.

while free rotation on a sphere of radius r is given by [31]

$$\text{EISF}(Q) = j_0^2(Qr), \quad (6b)$$

where $j_0(x) = \sin(x)/x$ is the spherical Bessel function. The EISF Q dependence for rotation about a C_2 molecular axis of methane is obtained using Eq. (6a) with $m = 2$ and $r = 0.89$ Å, while rotation about a C_3 molecular axis is obtained with $m = 3$ and $r = 1.03$ Å (using 1.09 Å and 109.5° as the bond length and bond angle for methane). The best fit at temperatures below the melting transition was obtained for rotation about the molecular C_2 axis, as shown in Fig. 3b. The discrepancy at low Q may be due to changes in the small-angle scattering caused by the addition of methane to the xerogel. The two-fold rotational symmetry of methane adsorbed onto the pores of the silica xerogel is in contrast to the nearly isotropic rotational diffusion motion in solid methane (phase I, $T > 20.4$ K [31]) or for submonolayer

methane adsorbed on graphite at 55 K [32]. The symmetry of the rotational motion is attributed to the relatively strong interactions between methane and surface silanol groups [35]. The preference for a two-fold rotation may suggest two weak hydrogen bonds between methane hydrogens and surface hydroxyl oxygens and/or possibly increased nearest neighbor interactions for the surface adsorbed monolayer.

The energy barriers to rotational and translational diffusion for methane adsorbed on SX4 were estimated by an Arrhenius plot of the QENS linewidth (which is proportional to the diffusion constant). The logarithm of the linewidth versus inverse temperature yields an activation energy for rotational diffusion (low temperature) and translational diffusion (high temperature). An Arrhenius plot for two Q values is shown in Fig. 4b. The resulting data is non-linear due to a distribution of rotational and translational energy barrier heights. The distribution

of diffusional barriers in the SX4 xerogel leads to a convolution of rotational and translational contribution to the QENS linewidth well below the melting temperature of methane. The solid curve through the QENS linewidth data in Fig. 4b is a fit to a bimodal distribution of activation energies, with $E_1 = 2.1$ kJ/mole and $E_2 = 0.17$ kJ/mole, with a weighting of 95% and 5% for the two components, respectively. These activation barriers can be compared with QENS results for methane trapped in small pore silica zeolites (e.g. ZSM-5, with 5.5 Å diameter channels [33,34]), as well as ordered silicate materials with larger pores (e.g. MCM-41, with 36 Å diameter [19]). The higher of the two xerogel barriers $E_1 = 2.1$ kJ/mole is less than the ~ 5 kJ/mole barrier reported for methane self diffusion in the silica zeolite ZSM-5. However, more facile translational diffusion in SX4 is reasonable given the larger 29 Å diameter pores of the xerogel versus the smaller 5.5 Å diameter channels of the ZSM-5 matrix [33,34]. The 2.1 kJ/mole activation energy may also include a rotational diffusion contribution from methane bound to silanol groups within the SX4 matrix, since relatively strong interactions have been reported between methane and surface silanol groups [35]. The lower xerogel energy barrier used in the bimodal fit, $E_2 = 0.17$ kJ/mole, is comparable to the 0.14 kJ/mole barrier attributed to methane rotational diffusion in MCM-41 at low temperature [19], indicating that the average rotational energy barrier for methane adsorbed in SX4 is not significantly different from the more ordered MCM-41 matrix.

4. Conclusions

The melting behavior of adsorbed methane within the pores of a silica xerogel formed at pH 4 was studied by quasielastic neutron scattering. The QENS data indicate that the surface of the silica xerogel yields a distribution of diffusional activation energies in the range 0.17 to 2.1 kJ/mole. This distribution is much broader than that reported for large pore semi-crystalline silicates (MCM-41) and small pore zeolites (ZSM-5). The EISF Q-dependence indicated that methane diffusion in SX4 is best fit by jump rotation about the molecular C_2 axis, indicative of significant methane silanol interactions. Future QENS measurements on dehydrated xerogel samples will be

able to quantify the effect of surface hydroxyls on the methane dynamics within SX4.

The porous structure and surface area of several silica xerogels (formed at pH 2, pH 4, pH 6), and an aluminosilica xerogel, were also characterized by SANS and by nitrogen adsorption isotherms. The mean pore size for these samples was observed to increase with the pH of the solution during polymerization of the silica matrix. The mean pore lengths were estimated by comparing the pore radii obtained from the adsorption isotherm data with the radius of gyration obtained from different analyses of the SANS measurements, indicating a tortuous pore structure for the xerogels.

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