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Adsorption and Diffusion Behavior of Ethane and Ethylene in Sol-Gel Derived Microporous Silica

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Abstract. High surface area silica (500 m^2/g) was synthesized by the sol-gel method from tetraethyl orthosilicate. The total porosity of the sample was 37% and most of the pores were well below 2 nm in size. The adsorption characteristics of ethylene and ethane in the silica were measured from 300–350 K by gravimetry, and Langmuir adsorption constants and enthalpies and entropies of adsorption were determined. Quasielastic neutron scattering was used to determine the translation and rotational diffusivities of both adsorbates from 200–270 K. Based on the adsorption and translational diffusion characteristics of ethylene and ethane, separation factors of 1.1–2 for olefin to paraffin are predicted.

Keywords: gas separation, adsorbents, diffusion

Introduction

The separation of small molecules similar in size and physical and chemical properties by inorganic membranes is very challenging. Often, the magnitude of the differences in the basic driving forces (Achyara and Foley, 2000; Hsieh, 1996; Ho and Sirkar, 1992) from Knudsen diffusion or molecular sieving are not sufficient to lead to large differences in the relative permeabilities of the species. In cases where separations are effected for small and similar species such as ethane/ethylene (Asaeda et al., 1994), propane/propylene (Asaeda et al., 1994; Nair et al., 1996a, 1996b), carbon dioxide/nitrogen (Keizer et al., 1988), or carbon dioxide/methane (Poshusta et al., 1999), a more complex mechanism may be invoked to explain the observed behavior. Such mechanisms may incorporate preferential adsorption of one species over another, pore mouth restriction, or preferential surface flow, and each of these mechanisms has been proposed for selected cases of species and membrane.

Inorganic microporous membranes have been fabricated for separating olefin/paraffin mixtures. Asaeda et al. (1994) reported on the use of silica membranes to separate ethane and ethylene and propylene and propane. Based on the pure component permeabilities, separation factors for olefin to paraffin of roughly 8–20 were observed at 35°C. Nair and co-workers (Nair et al., 1996a, 1996b), however, found that a pure silica

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membrane would only reproduce the Knudsen separation factor of 1.02 for propane/propylene mixtures. A silica membrane with a sorption-selective alumina layer was found to have a separation factor of 1.2 for ethylene over ethane (Uhlhorn et al., 1989), and a factor of 1.4–1.7 for propylene over propane (Nair et al., 1996a, 1996b; Uhlhorn et al., 1989). Both adsorption selectivity of olefin to paraffin and differences in the rates of surface diffusion of the species were used to explain the differences from the Knudsen values.

For a separation medium in the limit of very small pores, the separation factor, S, for a pair of species A and B can be represented as $S \propto D_A C_A/(D_B C_B)$, where D_i and C_i are the diffusivity and concentration, respectively, of species i. When bulk permeability measurements are made, neither D_i nor C_i is directly known. The concentration, however, can be determined from adsorption isotherm measurements. Direct measure of the diffusivity is more difficult to obtain, but quasielastic neutron scattering (QNS) (Bee, 1988; Benes et al., 2001; De Lara and Kahn, 1992; Gergidis et al., 2000; Jobic et al., 1992, 1995a, 1995b, 1997, 1998, 1999, 2000, Jobic, 2000; Stockmeyer, 1992; Springer, 1972) and nuclear magnetic resonance (NMR) (Jobic et al., 1995a, 1995b, 1998; Nivarthi and McCormick, 1995; Snurr and Kaerger, 1997) have been used to probe the dynamics of molecular motion in porous media. In principle, then, techniques exist to describe the terms appearing in the separation factor, although such measurements for the diffusivity are subject to interpretation (Kärger, 2003), depending on the manner in which they were performed. When independent measurements of D_i and C_i can be made, these values can be used to predict separation factors, which can then be compared with separation factors obtained from permeability measurements.

Quasielastic neutron scattering has been previously used to probe the diffusive motions of adsorbates in porous media. Much of the QNS work has focused on describing molecular motion in well-defined zeolitic structures (De Lara and Kahn, 1992; Jobic et al., 1992, 1997, 1998, 1999; Gergidis et al., 2000; Stockmeyer, 1992). For example, Stockmeyer (1992) examined the motion of molecular hydrogen in mordenite at temperatures between 90–120 K and determined translational and rotational self diffusivities of 2×10^{-7} cm^2/s and 2×10^{11} s^{-1}. De Lara and Kahn (1992) measured the self-diffusion coefficients of hydrogen and methane in zeolite A at 300 K. The motion of both molecules was described by a jump diffusion model, with the self diffusivity of hydrogen being 10^{-4} cm^2/s, which was orders of magnitude faster than that of methane. Jobic et al., (1992) studied the dynamics of ethane and propane in ZSM-5 by QNS and determined mean residence times, mean jump lengths, and rotational parameters. Both of these molecules exhibited very similar values for these quantities. Gergidis et al. (2000) have examined the diffusion of n-butane and methane in silicalite at 200 K and were able to determine the concentration dependence of the self diffusivity for both species. More recently, Jobic et al. (1997) determined the self and transport diffusivities of deuterium in NaX zeolites and showed that although the self diffusivity was relatively concentration independent, the transport diffusivity increased with increased molecular loading. Jobic et al. (1997) have also examined the unidirectional and single file diffusion of C_1–C_3 normal and cyclic alkanes. Hong and co-workers (Hong et al. 1991) have compared the diffusivities of ethane and ethylene in NaX zeolites, both for the individual species and when the two species were co-adsorbed. When both species were present, the diffusivity of ethylene was virtually unchanged whereas the diffusivity of ethane was reduced.

To a much lesser extent, the motion of adsorbates in non-crystalline porous solids has been examined (Jobic et al., 1995a, 1995b; Benes et al. 2001). The mobility of cyclohexane in silica at 300 K (Jobic et al., 1995b) was determined from QNS and led to measured translational and rotational self-diffusion coefficients of 10^{-6} cm^2/s and 10^{11} s^{-1}, respectively. A similar value of the self-diffusion coefficient for cyclohexane was obtained by the same authors (Jobic et al., 1995b) using pulsed-field gradient-NMR. Benes et al. (2001) determined a diffusivity of 10^{-4} cm^2/s for methane in microporous silica at 200 K. In addition, the authors used small angle X-ray scattering to determine the pores size distribution and found that the largest fraction of pore sizes in the silica was below 0.2 nm.

The focus of this work is to characterize the adsorption and diffusion behavior of ethane and ethylene in microporous silica derived from the sol-gel method. The adsorption behavior will be determined by gravimetric measurements; the enthalpy and entropy of adsorption will then be derived from these data. Quasielastic neutron scattering will be used to characterize the molecular motion of the molecules in the micropores of the silica in order to determine the rotational and translational diffusivities. An advantage of QNS that will be utilized is that the H-atom has a scattering cross section about 10 times greater than for deuterium. In experiments involving mixtures of ethylene and ethane, deuteration of one species will minimize its contribution to the measured signal relative to that of the protonated counterpart, and thus the diffusivity of one component can be characterized in the presence of the other. This feature allows us to probe the dynamics of molecular motion in microporous materials under conditions more closely corresponding to real separation environments where both species are present.

Experimental

The silica membrane material was prepared from a sol-gel synthesis route with 44 ml of tetraethyl orthosilicate in 70 ml of ethanol and 22 ml of water with 2 ml of concentrated HCl as the hydrolysant. The solution was mixed at 50°C and then gelled after 20 h at 50°C. After gelation, the samples were calcined in air at 300°C for two hours.

The nitrogen adsorption isotherms on the silica were performed after outgassing the sample at 120°C for 6 h. The adsorption isotherms of ethane and ethylene on the two materials were determined from gravimetric adsorption experiments with a microbalance. Prior to performing the measurements, the samples were outgassed at 170°C for 24 h under vacuum.

The QNS data were collected using the QENS instrument at the Intense Pulsed Neutron Source at Argonne National Laboratory (Bradley et al., 1988). This spectrometer provides an energy resolution of ~80 μeV (fwhm) and a range of momentum transfers, $0.35\ \text{Å}^{-1} < Q < 2.5\ \text{Å}^{-1}$. The spectrometer is typically sensitive to diffusive motions on time scales as long as 30×10^{-12} s (corresponding to a Lorentzian quasielastic broadening with hwhm of 20 μeV) and length scales d of $2.5\ \text{Å} < d < 20\ \text{Å}$. A 1 g sample of silica was contained in a 0.3 cm diameter by 10 cm long cylindrical holder made of aluminum. Prior to the QNS measurements, the sample was outgassed at 129°C for 3 h with a turbomolecular pump. The QNS runs were performed at 270 K, 235 K and 200 K. For the runs with only a single adsorbate, 0.655 (0.672) mmol of ethane (ethylene) was dosed into the sample cell at room temperature. For runs with a mixture of the gases, 0.656 mmol of deuterated ethane was added at room temperature to the 0.672 mmol of ethylene already present in the sample cell. Thus, for the QNS runs on the mixture, the loading in the sample cell was nearly twice that as compared to the QNS runs performed on the individual pure components; the individual loading of each adsorbate in the mixture, however, was nearly the same. Sample backgrounds were measured of the cell and of the evacuated silica. The data were normalized using the signal measured from a 6 mm diameter vanadium rod.

Results

Nitrogen adsorption on the sol-gel derived silica displayed a clear Type I isotherm without hysteresis (Lowell and Shields, 1984; Ruthven, 1984) and corresponds to a BET surface area of 519 m^2/g. The adsorption isotherm was further analyzed by the t-plot method and showed two distinct regions of linearity, from which it was determined that 97% of the micropores are below 2 nm in size. The Dubinin-Radushkevich equation (Ruthven, 1984) was used to determine a pore volume of 0.28 cm^3/g, which agrees well with the estimate of 0.30 cm^3/g obtained from the maximum uptake of nitrogen by physisorption. For a skeletal density of 2.2 g/cm^3 for silica, the pore volume implies a bulk density of 1.4 cm^3/g, which corresponds to 37% porosity.

To further characterize the pore size distribution, the nitrogen adsorption isotherm was analyzed by the MP method (Ruthven, 1984), and the results of this analysis are shown in Fig. 1, which indicates a pore size distribution predominantly below radii of 0.5 nm. Although use of the MP method is not fully justified on theoretical grounds for such small pores, the results do suggest that some fraction of the pores may be in the range of the molecular dimensions of ethylene and ethane, which have Van der Waals radii of 0.154 and 0.158 nm, respectively. The small pore size determined from the MP method is similar to the results obtained by small angle X-ray diffraction on microporous silica

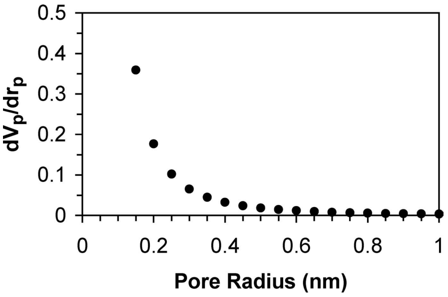

Figure 1. Pore size distribution of the sol-gel derived silica as determined by the MP method applied to nitrogen adsorption data.

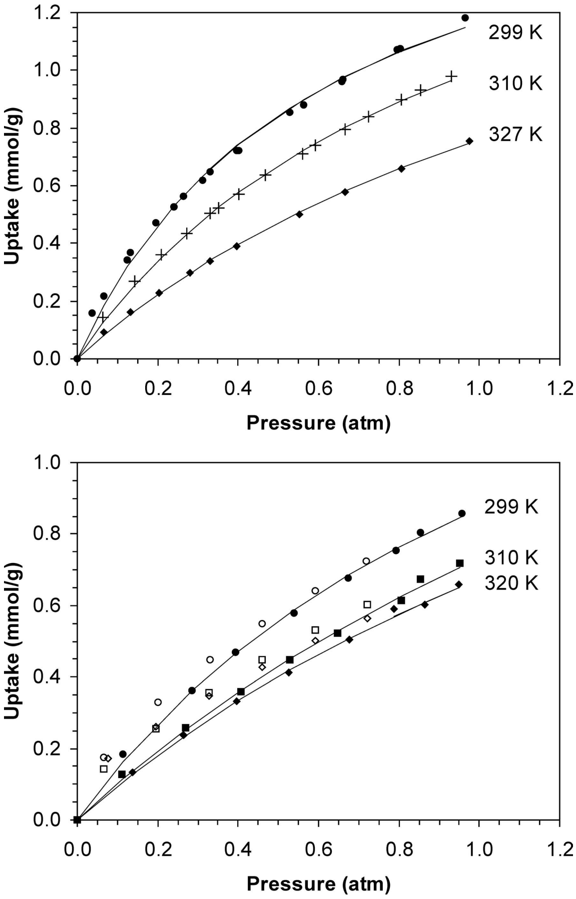

Figure 2. Adsorption isotherms of ethylene (*top panel*) and ethane (*bottom panel*) on silica at different temperatures. For ethane, the adsorption branch is indicated by filled symbols, and the desorption branch is indicted by open symbols.

Table 1. Langmuir constants, K, and monolayer uptakes, W_m, for adsorption of ethane and ethylene on silica.

	Ethylene			Ethane	
Temperature (K)	K (atm^{-1})	W_m (mmol/g)	Temperature (K)	K (atm^{-1})	W_m (mmol/g)
299	1.63	1.88	299	0.79	1.98
310	1.04	1.96	310	0.43	2.42
327	0.65	1.92	320	0.48	2.09

(Benes et al., 2001). Such small pore sizes have also been reported by others (de Lange et al., 1996; Elferink et al., 1996) for microporous materials synthesized by the sol-gel method.

The adsorption isotherms of ethylene and ethane on silica are shown in Fig. 2. The isotherms for ethylene exhibit adsorption behavior characteristic of Langmuir kinetics (see Table 1) and indicate no hysteresis between the adsorption and desorption branches. The adsorption isotherms for ethane are also shown in Fig. 2, and close inspection of the curves does indicate some hysteresis, especially at lower temperature. The Langmuir constants for the adsorption branch for ethane are also shown in Table 1. For an uptake of 1 mmol/g and a molecular radius of 0.15 nm, the projected coverage of the (planar) surface area of the silica is 10%; if the same calculation is performed based on single file loading of adsorbates in pores of cylindrical shape of radii nearly the same size as the adsorbates, then the coverage of the surface area by the projected size of the adsorbates is 20%. These two idealized treatments, which span a range of likely pore geometries, thus suggest a moderately crowded system.

The adsorption isotherms in Fig. 2 for ethylene were converted to isosteres in order to obtain the enthalpy and entropy of adsorption (Ruthven, 1984) as a function of coverage. For ethane, only the adsorption branch of the isotherm was used. Figure 3 shows that the heat of adsorption of ethylene is 25.5 kJ/mol and is independent of coverage. For ethane, the heat of adsorption of ethane is 17 kJ/mol at low coverage and decreases weakly with coverage. The isosteric heats of adsorption reported here for both adsorbates are consistent with other reported values of ~20 kJ/mol (Asaeda et al., 1994; Choudhary and Mayadevi, 1993a, 1993b; de Lange et al., 1996; Elferink et al., 1996; Yang and Kikkinides, 1995) for these species adsorbed on inorganic surfaces for which no strong chemical bonding occurs.

The entropy of adsorption for the two adsorbates as a function of coverage is shown in Fig. 4. For

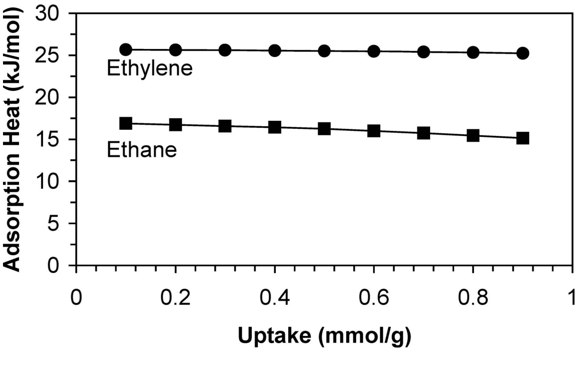

Figure 3. Adsorption enthalpy for ethane and ethylene on silica as a function of adsorbate loading.

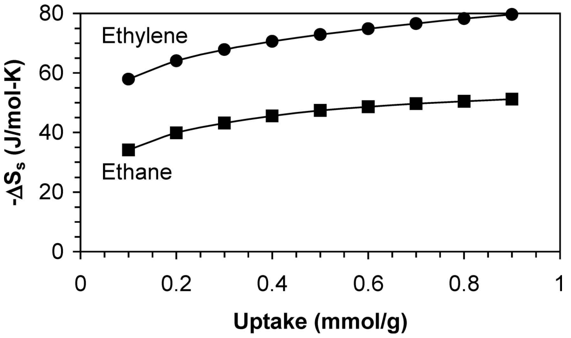

Figure 4. Adsorption entropy at 299 K for ethane and ethylene on silica as a function of adsorbate loading.

both adsorbates, the entropy of adsorption exhibits a very weak dependence (1–5% variation) with temperature, and for this reason, only the curves at 299 K are shown. The entropy of adsorption of both species increases in magnitude with increasing coverage, which implies more restriction, i.e., less degrees of freedom, as the adsorbate loading increases. The maximum magnitude of entropy decrease of 80 J/mol-K for ethylene at high coverage is very close to the value of the entropy change of vaporization at 1 atm of 80–88 J/mol-K (Green, 1997). This implies that at the maximum uptake, the ethylene has lost sufficient degrees of freedom to be similar, from the magnitude of the entropic change, to the liquid phase, although we cannot say definitively how the total entropy in the adsorbed phase is distributed among the configurational entropy and the rotational, vibrational, and translational modes.

Figure 5 shows the neutron scattering data collected from the ethane-containing sample at 200 K along with the background measurement of the aluminum sample cell and the adsorbate-free silica. The background was scaled by 0.98 to account for attenuation from adsorbate scattering, and this resulted in removal of all elastic scattering at higher Q values. The open circles with error bars in the figure are the signal remaining after subtraction of the scaled background. As Q increased, there was a clear increase in the width of the quasielastic peak, which is indicative of the continuous nature of the translational diffusion.

The subtracted neutron scattering data were analyzed in terms of two models: Model 1: a random three-dimensional diffusion model convoluted with an isotropic rotation about the molecule center-of-mass; and Model 2: a one-dimensional random diffusion model (Jobic, 2000) also convoluted with an isotropic rotation about the molecule center-of-mass (and powder averaged). In all the analyses, a radius of gyration of 1.55 Å was assumed. Unfortunately, the combination of the required addition of an extra delta-function to account for imperfect subtraction of the sample cell/silica signal and the poor statistics (limiting the line shape analysis) prohibited the unique selection of one model over the other and limited the maximum Q to which the data could be analyzed to approximately 1.5 Å^{-1}. This latter limitation made unique extraction of a rotational diffusion constant nearly impossible. The data were thus fit to the two models described above in two stages: in the first pass, the rotational time constant, τ_R, was allowed to vary freely for each sample/temperature combination. The uncertainties in τ_R for a given model were larger than the differences observed as a function of temperature or sample, although

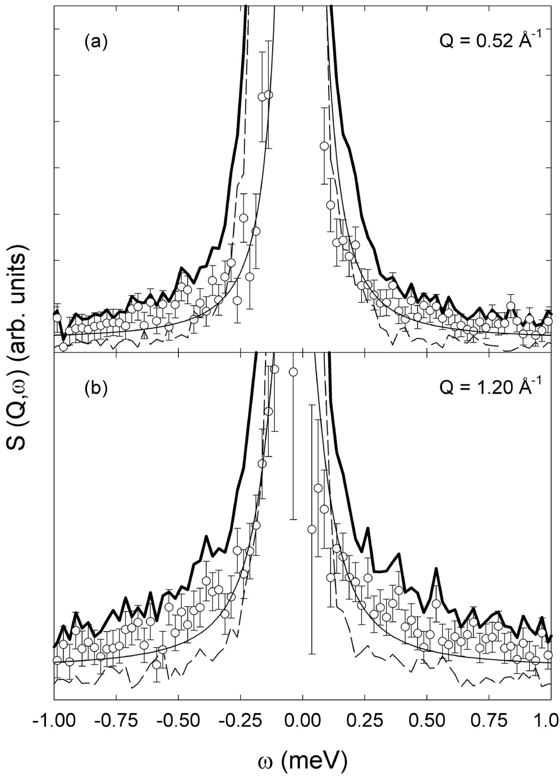

Figure 5. Neutron scattering data for ethane at 200 K at two momentum transfers. The heavy solid line is the signal collected with the ethane present, and the dashed line is the background signal. The open circles with the indicated uncertainties are the difference. The solid light line is a Lorentzian fit to the open circles and is present as a guide to the eye.

Table 2. Translational self-diffusion constants determined from analysis of the quasielastic neutron scattering data using the two models described in the text.

	Model 1 D_t 10^{-5} cm^2/sec	Model 2 D_t 10^{-5} cm^2/sec
Ethane		
200 K	0.43 ± 0.05	4.0 ± 0.1
235 K	2.90 ± 0.22	13.0 ± 1.3
270 K	5.3 ± 0.35	22.8 ± 2.0
Ethylene		
200 K	0.42 ± 0.07	2.6 ± 0.5
235 K	2.10 ± 0.25	11 ± 1.5
270 K	4.36 ± 0.40	16.9 ± 2.1
Ethylene in Mixture		
200 K	1.35 ± 0.11	5.8 ± 0.5
235 K	2.60 ± 0.16	12.8 ± 0.9

Model 1 is a random three-dimensional diffusion model while Model 2 is a one-dimensional random diffusion model.

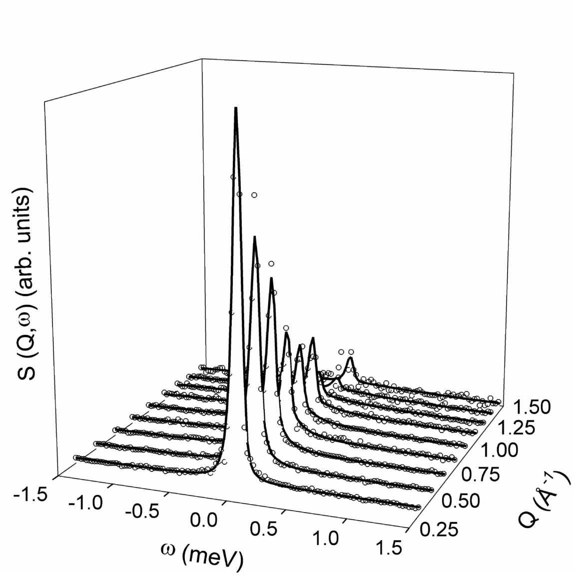

Figure 6. Neutron scattering data for ethane at 235 K with subtraction of the silica background. The heavy solid lines are fits to the entire spectrum using the random three-dimensional diffusion model described in the text.

the values observed using Model 2 were consistently larger than those obtained using Model 1. Because of this insensitivity, we chose to fit all the data by constraining the rotational motion to have the average measured value of $\tau_R = 0.48 \pm 0.07 \times 10^{-12}$ s (Model 1) and $0.65 \pm 0.12 \times 10^{-12}$ s (Model 2). The fitted values and uncertainties of the translational diffusion constants in Table 2 were insensitive to the actual constrained value of τ_R within the range of uncertainties in τ_R given above. Thus, over the Q-range examined here, the details of the rotational model did not strongly affect the translational diffusion constants.

Figure 6 shows the fits obtained for the ethane sample at 235 K using the random three-dimensional diffusion model. The model is capable of describing the data very well over a range of Q values. Similar agreement was obtained for ethylene. Figure 7 shows that when both species are adsorbed at 200 K, ethylene exhibits a considerably greater mobility than for ethylene adsorbed alone.

Table 2 summarizes the results of fitting the data to the two models described above. The translational self-diffusion constants, D_t, calculated using the one-dimensional model are considerably larger than those obtained using the three-dimensional model. This effect originates in performing the powder average of the one-dimensional diffusion scattering law (Jobic et al., 2000). The effective diffusion constant (D_t $\cos^2\theta$) appears smaller for channels which are oriented at an angle θ to the Q-vector of the experiment. As the average is performed, the model compensates by increasing the one-dimensional D_t relative to the value

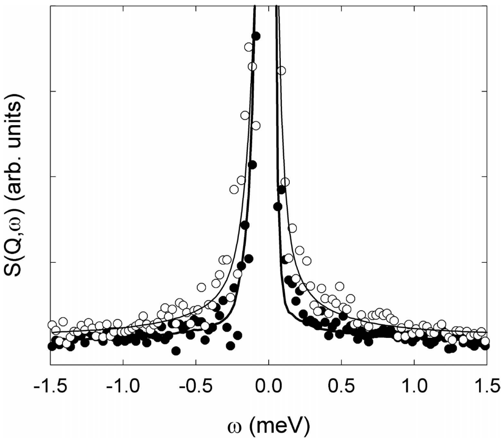

Figure 7. Neutron scattering data for ethylene (the silica background has been removed) at 200 K and a momentum transfer of 0.52 Å^{-1}. The data have been normalized to the same integrated intensity. The filled circles were collected from ethylene alone adsorbed on the silica while the open circles were collected from ethylene in the presence of deuterated ethane. The data clearly indicate that when ethane is present, ethylene exhibits a considerably greater mobility than ethylene by itself. The solid lines are fits to the data using the random three-dimensional diffusion model described in the text.

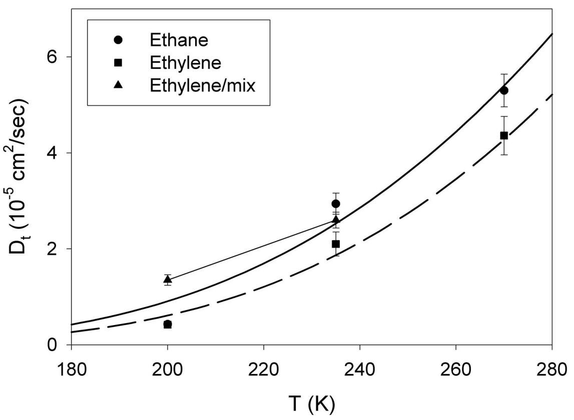

Figure 8. A summary of the translational diffusion coefficients derived from fits to the scattering data using the random three-dimensional diffusion model described in the text. At the lowest temperature (200 K), nearly the same diffusion coefficient is observed for both the pure ethane and pure ethylene. The heavy solid and dashed curves are Arrhenius fits to both the pure ethane and ethylene data. Similar activation energies are observed for both molecules, 11.5 ± 3 kJ/mole and 12.5 ± 2 kJ/mole, for ethane and ethylene respectively. Similar activation energies are also derived from fits using the one-dimensional diffusion model described in the text.

Table 3. Summary of the physical characteristics of the sol-gel derived silica with the adsorption and diffusion properties of ethylene and ethane from the three-dimensional diffusion model.

Property	Value	Units
Surface area of silica	519	m^2/g
Pore size of silica	$\ll$2	nm
Max. uptake ethylene (299 K)	1.2	mmol/g
Max. uptake ethane (299 K)	0.8	mmol/g
$-\Delta H_s$ ethylene	25	kJ/mol
$-\Delta H_s$ ethane	16	kJ/mol
$-\Delta S_s$ ethylene	60–80	J/mol-K
$-\Delta S_s$ ethane	35–50	J/mol-K
D_r ethylene	2.1×10^{12}	s^{-1}
D_r ethane	2.1×10^{12}	s^{-1}
D_t ethylene (235 K)	2.10×10^{-5}	cm^2/s
D_t ethane (235 K)	2.90×10^{-5}	cm^2/s
D_t ethylene in mix (235 K)	2.60×10^{-5}	cm^2/s
E_{diff} ethylene	12.5	kJ/mol
E_{diff} ethane	11.5	kJ/mol
E_{diff} ethylene in mix (235 K)	7	kJ/mol

determined using the three-dimensional diffusion model in order to fit the experimental line width.

Figure 8 shows the translational diffusion constants determined from the data using the three-dimensional model (Model 1) as a function of temperature. At low temperature, both adsorbates have nearly the same diffusivity, but at higher temperature, ethane appears to be diffusing more quickly. The limited amount of data for ethylene in the mixture suggests that it is diffusing slightly more rapidly than for pure ethylene. It should also be noted that for ethylene in the mixture, the total adsorbate loading may be nearly doubled as compared to the loading when ethylene is adsorbed alone. Similar activation energies, E_{diff}, of 11.5 ± 3 kJ/mole and 12.5 ± 2 kJ/mole are observed for ethane and ethylene respectively; for ethylene in the mixture, the activation energy for diffusion of ~7 kJ/mol is lower than for the pure component. This presumably arises from either adsorbate-adsorbate interactions or from competition for adsorption sites at higher loadings.

Discussion

A summary of the physical characteristics of the sol-gel silica and the adsorption and diffusion properties of ethylene and ethane in the silica is presented in Table 3. The picture that emerges from the results of these multiple characterization techniques is that the sol-gel derived silica is a high surface area material with the majority of pores below 1 nm, and some pores may be in the range of the size of the adsorbates. Both ethylene and ethane exhibit qualitatively similar adsorption behavior, except that ethane shows hysteresis.

In terms of diffusion behavior, both ethane and ethylene exhibit three-dimensional (Model 1) D_t values of about 5% of their respective bulk values at 200 K as measured by NMR at or near saturated vapor pressure conditions (Arends et al., 1981; Gaven et al., 1962). At 235 K and 270 K, the measured values of D_t are about 20 and 13% of the bulk values for ethane and ethylene, respectively. As expected, the influence of the confining pores significantly lowers the self-diffusion coefficient of each species relative to bulk values. QNS has been previously used to study the motion of ethane in zeolite ZSM-5 at 300 K with a reported diffusion coefficient of about 1–3 × 10^{-5} m^2/sec (depending on loading) using a three-dimensional jump-diffusion scattering law to analyze the data (Jobic et al., 1992). This is slightly slower than the translational motion for ethane observed in this study on microporous silica at 270 K.

However, a comparison of the mobility of methane shows an increase in D_t of about 5 times in microporous silica relative to ZSM-5 (Benes et al., 2001). It is thus reasonable to assume that ethane will also exhibit an enhanced mobility in silica relative to ZSM-5.

Hong et al. (1991) have examined the diffusivities of ethane and ethylene in NaX zeolites at 293 K. When adsorbed separately, the diffusivity of ethane is an order of magnitude larger than that of ethylene. When coadsorbed, however, the diffusivity of ethylene is nearly unchanged whereas that of ethane is reduced by roughly a factor of two. This behavior was attributed to interactions between the adsorbates. In this work, the effect of coadsorption on the diffusivity is much less pronounced; we do observe, however, that the diffusivity of ethylene is slightly enhanced in the mixture relative to that of the pure component.

The values of uptake (concentration) and diffusivities determined in this work for the pure components can be used to predict separation factors of 1.1–2 for ethylene to ethane. Such modest values are consistent with the small separation factors for olefin to paraffin reported by others (Nair et al., 1996a, 1996b; Uhlhorn et al., 1989) based on permeability measurements. Based on the small change in the diffusivity of ethylene in the presence of ethane, no large differences would be expected for the ratio of diffusivities for the pure components as compared to when both species are present; thus, the separation factors would not be expected to change by much as a consequence of this small effect. At high concentrations, however, where the effects of molecular crowding are more pronounced, competitive adsorption and adsorbate-adsorbate interactions may lead to different behavior. This may be why the activation energy for ethylene in the presence of ethane is less than for ethylene adsorbed alone, although this does not manifest itself dramatically in an increase in the translational diffusivity of the olefin.

Conclusions

The adsorption and diffusion characteristics of ethane and ethylene in sol-gel derived silica have been determined. Based on nitrogen adsorption measurements, the silica is a moderately high surface area material with 37% porosity. Most of the pores are less than 2 nm in size and a fraction of the pores may be on the size of the dimensions of the adsorbates. The heat of adsorption of ethylene is greater than that of ethane, and both are nearly independent of loading. Both adsorbates experience a decrease in adsorption entropy with increasing loading. From the quasielastic neutron scattering measurements, the translational diffusion behavior of the two adsorbates is an activated process. Both random one-dimensional and three-dimensional translational diffusivities could be extracted from the neutron data, but it was not possible to unambiguously determine which model was better. Based on the translational and adsorption behavior of the individual adsorbates, modest separation factors of up to 2 are predicted. When ethylene was co-adsorbed with ethane, the activation energy for diffusion was reduced, but the overall translational mobility was not significantly different than when ethylene was adsorbed alone.

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References

Achyara, M. and H.C. Foley, "Transport in Nanoporous Carbon Membranes: Experiments and Analysis," *AIChE J.*, **46**, 911–922 (2000).

Arends, B., K.O. Prins, and N.J. Trappeniers, "Self-Diffusion in Gaseous and Liquid Ethylene," *Physica*, **107A**, 307–318 (1981).

Asaeda, M., A. Yamamichi, M. Satoh, and M. Kamakura, "Preparation of Porous Silica Membranes for Separation of Propylene/Propane Gaseous Mixtures," in *Inorganic Membranes: ICIM3 '94:* Proceedings of the Third International Conference on Inorganic Membranes: Worcester, MA, July 10–14, 1994.

Bée, M., *Quasielastic Neutron Scattering*, Adam Hilger, Bristol, 1988.

Benes, N.E., H. Jobic, and H. Verweij, "Quasi-Elastic Neutron Scattering Study of the Mobility of Methane in Microporous Silica," *Microporous & Mesoporous Mater.*, **43**, 147–152 (2001).

Bradley, K.F., S.H. Chen, T.O. Brun, R. Kleb, W.A. Loomis, and J.M. Newsam, "The Design and Performance of QENS, a Medium Resolution, Inverted Geometry, TOF Quasielastic and Inelastic Spectrometer at IPNS," *Nucl. Instr. and Meth.*, **A240**, 78–89 (1988).

Choudhary, V.R. and S. Mayadevi, "Adsorption of Methane, Ethane, Ethylene, and Carbon Dioxide on X, Y, L, and M Zeolites Using a Gas Chromatography Pulse Technique," *Separation Sci. & Technol.*, **28**, 1595–1607 (1993a).

Choudhary, V.R. and S. Mayadevi, "Adsorption of Methane, Ethane, Ethylene, and Carbon Dioxide on High Silica Pentasil Zeolites and Zeolite Like Materials Using Gas Chromatography Pulse Technique," *Separation Sci. & Technol.*, **28**, 2197–2209 (1993b).

De Lange, R.S. A., J.H.A. Hekkink, K. Keizer, and A.J. Burggraaf, "Microstructural Properties of Non-Supported Microporous Ceramic Membrane Top-Layers Obtained by the Sol-Gel Process," *J. Non-Cryst. Sol.*, **195**, 203–217 (1996).

De Lara, E.C. and R. Kahn, "Diffusivity of Hydrogen and Methane Molecules in A Zeolites: Neutron Scattering Measurements and Comparison," *Zeolites*, **12**, 256–260 (1992).

Elferink, W.J., B.N. Nair, R.M. de Vos, K. Keizer, and H. Verweij, "Sol-Gel Synthesis and Characterization of Microporous Silica Membranes: II. Tailor-Making Porosity," *J. Coll. Interf. Sci.*, **180**, 127–134 (1996).

Gaven, J.V., W.H. Stockmayer, and J.S. Waugh, "Self-Diffusion and Impurity-Controlled Proton Relaxation in Liquid Ethane," *J. Chem. Phys.*, **37**, 1188–1191 (1962).

Gergidis, L.N., D.N. Theodorou, and H. Jobic, "Dynamics of *n*-Butane-Methane Mixtures in Silicalite, Using Quasielastic Neutron Scattering and Molecular Dynamics Simulations," *J. Phys. Chem. B*, **104**, 5541–5552 (2000).

Green, D.W. (Ed.), *Perry's Chemical Engineers' Handbook,* McGraw-Hill, New York, 1997.

Ho, W.S. and K.K. Sirkar (Eds.), *Membrane Handbook*, Van Nostrand Reinhold, New York, 1992.

Hong, U., J. Kärger, and H. Pfeifer, "Selective Two-Component Self-Diffusion Measurement of Adsorbed Molecules by Pulsed Field Gradient Fourier Transform NMR," *J. Am. Chem. Soc.*, **113**, 4812–4815 (1991).

Hsieh, H.P., *Inorganic Membranes for Separation and Reaction*, Elsevier, New York, 1996.

Jobic, H., "Diffusion Studies Quasi-Elastic Neutron Scattering," in *Recent Advances in Gas Separation by Microporous Ceramic Membranes*, N.K. Kanellopoulos, ed., Elsevier, New York, 109 (2000).

Jobic, H., M. Bee, J. Karger, C. Balzer, and A. Julbe, "Measurement of the Diffusivity of Benzene in Microporous Silica by Quasi-Elastic Neutron Scattering and NMR Pulsed-Field Gradient Technique," *Adsorption*, **1**, 197–201 (1995a).

Jobic, H., M. Bee, J. Karger, R.S. Vartapetian, C. Balzer, and A. Julbe, "Mobility of Cyclohexane in a Microporous Silica Sample: A Quasi-Elastic Neutron Scattering and NMR Pulsed-Field Gradient Technique Study," *J. Membrane Sci.*, **108**, 71–78 (1995b).

Jobic, H., M. Bee, and G.J. Kearley, "Dynamics of Ethane and Propane In Zeolite ZSM-5 Studied by Quasi-Elastic Neutron Scattering," *Zeolites*, **12**, 146–151 (1992).

Jobic, H., H. Ernst, W. Heink, J. Karger, A. Tuel, and M. Bée, "Diffusion of Ammonia in Silicalite Studied by QENS and PFG NMR," *Microporous & Mesoporous Mater.*, **26**, 67–75 (1998).

Jobic, H., A.N. Fitch, and J. Combet, "Diffusion of Benzene in NaX and NaY Zeolites Studied by Quasi-Elastic Neutron Scattering," *J. Phys. Chem. B*, **104**, 8491–8497 (2000).

Jobic, H., K. Hahn, J. Kärger, M. Bée, A. Tuel, M. Noack, I. Girnus, and G.J. Kearley, "Unidirectional and Single-File Diffusion of Molecules in One-Dimensional Channel Systems. A Quasi-Elastic Neutron Scattering Study," *J. Phys. Chem B*, **101**, 5834–5841 (1997).

Jobic, H., J. Karger, and M. Bée, "Simultaneous Measurement of Self- and Transport-Diffusivities in Zeolites," *Phys. Rev. Lett.*, **82**, 4260–4263 (1999).

Kärger, J., "Measurement of Diffusion in Zeolites—A Never Ending Challenge?," *Adsorption*, **9**, 29–35 (2003).

Keizer, K., R.J.R. Uhlhorn, R.J. Van Huren, and A.J. Burggraaf, "Gas Separation Mechanisms in Microporous Modified Gamma -Al_2O_3 Membranes," *J. Membrane Sci.*, **39**, 285–300 (1988).

Lowel, S. and J.E. Shields, *Powder Surface Area and Porosity*, Chapman Hall, New York, 1984.

Nair, B.N., K. Keizer, W.J. Elferrink, M.J. Gilde, Verweij, H., and A.J. Burggraaf, "Synthesis, Characterization and Gas Permeation Studies on Microporous Silica and Alumina-Silica Membranes for Separation of Propane and Propylene," *J. Membrane Sci.*, **116**, 161–169 (1996a).

Nair, B.N., K. Keizer, H. Verweij, and A.J. Burggraaf, "Surface Selective Approach to Separation of Propylene from Propane," *Separation Sci. and Technol.*, **31**, 1907–1914 (1996b).

Nivarthi, S.S. and A.V. McCormick, "Diffusion of Coadsorbed Molecules in Zeolites. A pulsed Field Gradient NMR Study," *J. Phys. Chem.*, **99**, 4661–4666 (1995).

Poshusta, J.C., R.D. Nobel, and J.L. Falconer, "Temperature and Pressure Effects on CO_2 and CH_4 Permeation Through MFI Zeolites," *J. of Membrane Sci.*, **160**, 115–125 (1999).

Ruthven, D.M., *Principles of Adsorption and Adsorption Processes*, John Wiley, New York, 1984.

Snurr, R.Q. and J. Kaerger, "Molecular Simulations and NMR Measurements of Binary Diffusion in Zeolites," *J. Phys. Chem. B*, **101**, 6469–6473 (1997).

Springer T., in *Quasielastic Neutron Scattering for the Investigation of Diffusive Motions in Solids and Liquids*, G. Hohler, Ed., Springer Tracts in Modern Physics 64, Springer-Verlag, Berlin, pp. 1–100 (1972).

Stockmeyer, R. "Diffusive Motion of Hydrogen in Mordenite Studied by Quasi-Elastic Neutron Scattering," *Zeolites*, **12**, 251–255 (1992).

Uhlhorn, R.J. R., H.B.J. Huis In't Veld, K. Keizer, and A.J. Burggraaf, "High Permselectivities of Microporous Silica-Modified γ-Alumina Membranes," *J. Mat. Sci. Lett.*, **8**, 1135–1138 (1989).

Yang, R.T. and E.S. Kikkinides, "New Sorbents for Olefin/Paraffin Separations by Adsorption Via π-Complexation," *AIChE J.*, **41**, 509–517 (1995).