Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Liquid-Phase Sorption of Higher Alkanes and Alkenes in Zeolite NaZSM-5 at 10, 30, and 50°C

R. V. Jasra[a]; N. V. Choudary[a]; S. G. T. Bhat[a]; A. G. Patel[b]; N. Subrahmanyam[b]
[a] RESEARCH CENTRE INDIAN PETROCHEMICALS CORPORATION LTD., VADODARA, INDIA [b] DEPARTMENT OF CHEMICAL ENQINEER1NG, FACULTY OF TECHNOLOGY M.S. UNIVERSITY, VADODARA, INDIA

To cite this Article Jasra, R. V. , Choudary, N. V. , Bhat, S. G. T. , Patel, A. G. and Subrahmanyam, N.(1997) 'Liquid-Phase Sorption of Higher Alkanes and Alkenes in Zeolite NaZSM-5 at 10, 30, and 50°C', Separation Science and Technology, 32: 9, 1571 — 1587

To link to this Article: DOI: 10.1080/01496399708004067
URL: http://dx.doi.org/10.1080/01496399708004067

SEPARATION SCIENCE AND TECHNOLOGY, 32(9), pp. 1571–1587, 1997

Liquid-Phase Sorption of Higher Alkanes and Alkenes in Zeolite NaZSM-5 at 10, 30, and 50°C*

R. V. JASRA, N. V. CHOUDARY, and S. G. T. BHAT†
RESEARCH CENTRE
INDIAN PETROCHEMICALS CORPORATION LTD.
VADODARA, 391 346, INDIA

A. G. PATEL and N. SUBRAHMANYAM
DEPARTMENT OF CHEMICAL ENQINEERING
FACULTY OF TECHNOLOGY
M.S. UNIVERSITY BARODA
VADODARA, 390 002, INDIA

ABSTRACT

Adsorption and diffusion of normal alkanes and alkenes having carbon numbers from C8 to C15 have been measured in the liquid phase from a nonadsorbing solvent (trimethyl benzene) in zeolite NaZSM-5 at 10, 30, and 50°C. The diffusion coefficients show a sharp decrease for molecules whose carbon chain length is larger than the channel length of the zeolite. The adsorption isomers of octane have also been studied to observe the effect of minor structural changes in molecular shape on adsorption properties in the zeolite. The observed adsorption capacity data have been explained in terms of molecular packing in zeolite straight and sinusoidal channels and channel intersections.

INTRODUCTION

Despite its wide use in the hydrocarbon industry, there is limited literature on the adsorption and diffusion of hydrocarbons in zeolite ZSM-5 (1–7). Furthermore, the reported studies are largely confined to lower

---

* IPCL Communication 308.

† To whom correspondence should be addressed.

hydrocarbons, i.e., normal hexane. Jacobs et al. (1), from their adsorption studies on a wide range of normal alkanes in zeolite ZSM-5, concluded that for large alkanes (C_6–C_8) and short-chain iso-alkanes (C_4–C_5) the straight pores of the zeolite are filled with two molecules of alkanes occupying each intersection of the straight and sinusoidal pores. However, for C_8–C_9 carbon number normal alkanes, adsorption occurs in zigzag pores. It has also been reported that the molecular dimensions do not allow accommodation of two molecules per intersection. However, these studies were carried out at a higher temperature (200°C), and it would be interesting to observe whether this packing pattern is followed at a lower temperature. Richards and Rees (2), from the adsorption of ethane, propane, *n*-butane, and *n*-hexane in ZSM-5, proposed a model for the packing of adsorbed molecules inside the zeolite channels. It is worthwhile to study the packing of normal alkanes higher than C_6 to verify the packing model proposed (2). To observe the effect of a double bond as well as carbon chain length on the adsorption behavior, adsorption and diffusion of C_8 to C_{15} carbon number alkanes and alkenes in NaZSM-5 were measured and are reported.

Zeolite ZSM-5, owing to the presence of molecular-sized channels throughout the crystalline structure, presents an interesting substrate in which to explore the effect of minor structural variations of the adsorbate molecules on adsorption characteristics. Cavalcante and Ruthven (4), from a study of branched and cyclic hexane isomers, showed that adsorption equilibrium follows the trend double-branched < single-branched, cyclic alkanes. In the present study we also report the adsorption of a number of octane isomers which were studied to observe the effect of methyl substitution in the carbon chain on adsorption packing in the zeolite channel.

EXPERIMENTAL

The zeolite NaZSM-5 (SiO_2/Al_2O_3 ratio of 75) used was a commercial powder sample from CATAD Division of Indian Petrochemicals Corporation Ltd., India. Vapor-phase adsorptions of water, benzene, and hexane, as measured by a McBain quartz spring balance at 30°C and shown in Fig. 1, reflect the hydrophobicity of the zeolite surface. The average crystallite size as determined by a scanning electron microscope (Jeol, JSM 35C) was 3.8 × 2.9 μm.

The normal alkanes used were of high purity grade from E. Merck and Fluka A.G. The normal alkenes used were from Gulf Oil Company. These chemicals were used without further purification.

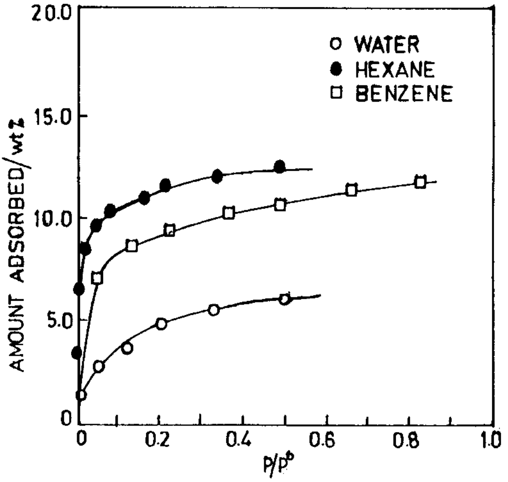

FIG. 1 Vapor-phase adsorption of water, benzene, and hexane measured.

The method used for the liquid-phase sorption uptake measurements is described in detail elsewhere (8). Adsorption was measured in a glass cell (ca. 5 mL) closed by means of a silicone rubber septum and a screw cap having a hole at the center. The zeolite sample was activated by heating at 350°C for about 8 hours in a glass reactor under a dry nitrogen purge. The activated zeolite sample (ca. 0.5 g) was transferred to the glass cell in a hot condition and the screw cap was closed. The amount of zeolite taken was determined by weighing the cell after transferring the zeolite. A known amount of the adsorbate solution in a nonadsorbing solvent, 1,3,5-trimethyl benzene, was injected into the cell. The experimental cell was then kept in a constant temperature water bath (Julabo SW1, Germany) maintained at the required temperature (±0.05°C). The mixture was regularly shaken to dissipate any heat evolved during adsorption. For measurements of equilibrium adsorption, the composition of the liquid mixture was determined after 24 hours. In the case of adsorption kinetic measurements, the composition of the solution was determined at regular time interval by analysis of the mixture withdrawn by means of a microsyringe. All the analyses were done with a gas chromatograph (Varian Vista 6500) having an OV 101 (3 mm × 500 mm) column and a thermal conductivity detector with hydrogen (flow rate, 30 mL/min) as the carrier gas. The errors in GC analysis were within ±0.5%.

The amount and the concentration of the solution were so chosen during kinetic measurements that the amount of adsorbing component in the solution was always in large excess, larger than that which was required to saturate the adsorbent. This was done to minimize errors in adsorption rates due to any change in adsorbate concentration during the experiment.

RESULTS AND DISCUSSION

Adsorption of Normal Alkanes and Alkenes

Adsorption isotherms of *n*-octane, *n*-decane, *n*-undecane, *n*-dodecane, *n*-tetradecane, and *n*-pentadecane in ZSM-5 at 10, 30, and 50°C measured in the liquid phase from a nonadsorbing solvent (trimethyl benzene) are of type I, typical of adsorption in micropores. The experimental adsorption data are given in Table 1. The isotherms show very good fit in all cases, showing 0.01 to 0.60 standard deviation. The saturation equilibrium adsorption capacities (V_m) for these molecules obtained from the Langmuir fit are given in Tables 2 and 3 (in column 2). To have a comparison of the adsorbed state with the liquid state, the amount of adsorbate required to completely saturate the zeolite channel volume was calculated by using the liquid density of the adsorbate. The calculated data are also given in Tables 2 and 3. The channel volume of the ZSM-5 zeolite crystals taken for these calculation was 0.19 cm^3/g (9). It was suggested by Dubinin (10) that the molar volume in the adsorbed state between normal boiling point and the critical point of a molecule may be calculated by using the following equation:

$$V^* = V_B + \frac{T - T_B}{T_c - T_B}(b - V_B) \qquad (1)$$

where V^* and V_B are the molar volumes at temperature T and at boiling point T_B respectively. T_c is the critical temperature, and b is the van der Waals constant. The theoretical saturation concentration for NaZSM-5 zeolite, assuming 100% occupancy of the free voidage, is given by the expression

$$N_0 = 0.19/V^* \qquad (2)$$

The theoretical saturation adsorption capacities were calculated for all the compounds using the above equations and are given in Tables 2 and 3. From these data the following observations can be made:

1. The experimentally observed saturation adsorption values are less (0.8 to 3.6%) than those calculated assuming adsorbed-state packing similar to liquid-state packing and show much lower values (3.5 to

TABLE 1
Adsorption Isotherm Data of Paraffins in NaZSM-5

c (mmol·g^{-1})	*q* (mmol·g^{-1})	*c* (mmol·g^{-1})	*q* (mmol·g^{-1})	*c* (mmol·g^{-1})	*q* (mmol·g^{-1})
n-Octane					
10°C		30°C		50°C	
0.212	0.816	0.197	0.858	0.197	0.858
0.533	0.907	0.528	0.918	0.554	0.896
1.073	0.943	1.074	0.943	1.074	0.916
1.619	0.922	1.619	0.926	1.622	0.907
2.414	1.151	2.430	1.076	2.439	1.035
4.033	1.058	4.047	0.969	4.054	0.969
6.290	1.130	5.195	0.946	5.204	0.884
		6.885	0.983	6.890	0.920
n-Undecane					
10°C		30°C		50°C	
0.042	0.489	0.042	0.489	0.042	0.489
0.125	0.862	0.146	0.799	0.148	0.790
1.125	0.870	0.597	0.829	0.609	0.789
1.765	0.837	1.162	0.820	1.171	0.776
2.401	0.786	1.788	0.719	1.793	0.760
3.688	0.794	2.418	0.711	2.426	0.745
		3.691	0.740	3.726	0.753
n-Dodecane					
10°C		30°C		50°C	
0.327	0.603	0.036	0.721	0.025	0.376
0.997	0.740	0.373	0.501	0.039	0.413
2.056	0.961	0.628	0.541	0.331	0.594
3.398	0.694	0.863	0.760	0.573	0.520
3.683	0.653	1.012	0.668	0.879	0.727
3.740	0.809	2.074	0.899	4.683	0.664
4.447	0.938	3.365	0.674		
		4.447	0.838		
n-Tetradecane					
10°C		30°C		50°C	
0.008	0.769	0.156	0.681	0.494	0.584
0.156	0.692	0.500	0.644	1.978	0.560
0.461	0.798	0.480	0.725	3.942	0.584
0.481	0.719	1.242	0.750	0.163	0.669
0.568	0.728	2.550	0.877		

(*continued*)

TABLE 1. Continued

c (mmol·g^{-1})	q (mmol·g^{-1})	c (mmol·g^{-1})	q (mmol·g^{-1})	c (mmol·g^{-1})	q (mmol·g^{-1})
1.227	0.806	3.153	0.798		
1.427	0.599	1.965	0.629		
1.958	0.660	2.954	0.559		
2.948	0.609	3.932	0.589		
3.509	0.842				
3.926	0.730				
		n-Pentadecane			
10°C		30°C		50°C	
0.008	0.258	0.017	0.258	0.033	0.258
0.017	0.509	0.324	0.560	0.333	0.536
0.315	0.585	1.101	0.651	0.695	0.583
0.687	0.607	1.755	0.533	1.146	0.563
1.090	0.673	2.700	0.612	1.616	0.502
1.728	0.603	3.641	0.759	1.728	0.608
2.683	0.683	1.721	0.630	2.914	0.491
3.658	0.763			3.644	0.759
1.692	0.706				
		2,2,4-Trimethylpentane			
10°C		30°C		50°C	
0.394	0.033	0.398	0.019	0.390	0.044
0.704	0.019	0.788	0.021	0.771	0.079
1.021	0.046	1.047	0.047	1.017	0.086
1.847	0.104	5.230	0.048		
3.529	0.237				
		2,3,4-Trimethylpentane			
10°C		30°C		50°C	
0.447	0.012	0.450	0.008	0.449	0.005
1.072	0.011	1.062	0.041	1.064	0.033
2.702	0.014	2.689	0.048	1.720	0.052
4.222	0.054	4.222	0.056	2.689	0.045
		4.730	0.080		
		4-Methylheptane			
10°C		30°C		50°C	
0.605	0.030	0.607	0.020	0.609	0.014
0.831	0.213	0.808	0.295	0.871	0.072
1.518	0.220	1.520	0.212	1.521	0.205
4.320	0.279	4.346	0.280	4.117	0.257

TABLE 1. Continued

c (mmol·g^{-1})	q (mmol·g^{-1})	c (mmol·g^{-1})	q (mmol·g^{-1})	c (mmol·g^{-1})	q (mmol·g^{-1})
4.917	0.226				
5.320	0.415				
		2,5-Dimethylhexane			
10°C		30°C		50°C	
0.179	0.617	0.168	0.672	0.175	0.624
0.666	0.581	0.748	0.835	0.747	0.784
0.889	0.556	1.018	0.660	0.984	0.683
0.935	0.683	1.659	0.886	1.642	0.868
1.600	0.710	2.462	0.852		
3.165	0.727	3.268	0.789		
		6.330	0.940		
		1-Octene			
10°C		30°C		50°C	
0.048	0.916	0.044	0.929	0.041	0.940
0.386	1.169	0.422	1.049	0.397	1.042
1.607	0.913	1.597	0.960	0.903	1.103
5.185	1.135	2.489	1.034	2.489	1.029
		1-Undecene			
10°C		30°C		50°C	
0.044	0.798	0.289	0.806	0.045	0.794
0.386	0.815	0.662	0.793	0.667	0.778
0.659	0.804	1.203	0.757	1.210	0.723
1.201	0.772	1.794	0.709	1.801	0.679
1.788	0.740	2.449	0.672	2.453	0.652
2.447	0.681	3.720	0.923	3.737	0.859
3.720	0.955	5.015	0.729		
5.014	0.736				
		1-Dodecene			
10°C		30°C		50°C	
0.026	0.653	0.027	0.650	0.027	0.650
0.293	0.697	0.295	0.689	0.297	0.682
1.072	0.690	1.072	0.690	1.083	0.641
1.632	0.763	1.079	0.653	1.634	0.757
2.242	0.791	1.629	0.776	2.258	0.720
3.428	0.799	2.242	0.792	3.429	0.786
4.660	0.979	4.661	0.974	4.667	0.909

(*continued*)

TABLE 1. Continued

c (mmol·g^{-1})	q (mmol·g^{-1})	c (mmol·g^{-1})	q (mmol·g^{-1})	c (mmol·g^{-1})	q (mmol·g^{-1})
		1-Tetradecene			
		30°C			
		0.017	0.603		
		0.171	0.788		
		0.371	0.732		
		0.849	0.762		
		1.358	0.885		
		3.188	0.910		
		4.007	0.884		
		4.018	0.908		

TABLE 2
Adsorption Data for Alkanes in NaZSM-5

	Equilibrium capacity (V_m) (mmol·g^{-1})		
		Calculated	
Adsorbate	Experimental[a]	Density	Dubinin
	At 10°C		
n-Octane	1.0840	1.1820	1.2499
n-Undecane	0.8479	0.9086	0.9542
n-Dodecane	0.8357	0.8428	0.8841
n-Tetradecane	0.7229	0.7367	0.8224
n-Pentadecane	0.6695	0.6936	0.7797
	At 30°C		
n-Octane	0.9856	1.1552	1.1671
n-Undecane	0.7840	0.9030	0.9232
n-Dodecane	0.7008	0.9030	0.9232
n-Tetradecane	0.6405	0.6811	0.7524
	At 50°C		
n-Octane	0.9451	1.1284	1.1324
n-Undecane	0.7820	0.8726	0.8941
n-Dodecane	0.6466	0.8109	0.8390
n-Tetradecane	0.6133	0.7110	0.7666
n-Pentadecane	0.6031	0.6688	0.7269

[a] Equilibrium adsorption capacity obtained by fitting experimental data into Langmuir equation.

TABLE 3
Adsorption Data for Alkenes in NaZSM-5

Adsorbate	Equilibrium capacity (V_m) (mmol·g^{-1})		
		Calculated	
	Experimental[a]	Density	Dubinin
	At 10°C		
n-Octene	1.0770	1.2248	1.2592
n-Undecene	0.7879	0.9333	1.3236
n-Dodecene	0.7538	0.8643	1.1059
	At 30°C		
n-Octene	1.0177	1.1964	1.2174
n-Undecene	0.7700	0.9146	1.2461
n-Dodecene	0.7421	0.8477	1.0421
n-Tetradecene	0.7121	0.7393	1.3072
	At 50°C		
n-Octene	1.1152	1.1681	1.1782
n-Undecene	0.7542	0.8959	1.1771
n-Dodecene	0.7217	0.8313	0.9854

[a] Equilibrium adsorption capacity obtained by fitting experimental data into Langmuir equation.

16.5%) than those estimated using Dubinin's equation for adsorbed phase molar volume. The deviations between the calculated and experimentally observed values increase with increasing temperature. For example, these deviations vary as 3–16, 6–20, and 13–30% at 10, 30, and 50°C, respectively. Further, the deviations also show an increasing trend with an increase in the carbon number of the adsorbate molecules.

2. The measured adsorption saturation values for alkenes also show lower values than the calculated ones, as seen in the Table 3. Comparing these deviations with those of alkanes, the deviations are higher in the case of alkenes. However, the deviation do not show as much dependence on temperature as seen for alkanes.

These observations suggest that the packing of the molecules in the adsorbed phase for alkenes and alkanes in ZSM-5 channels is not as dense as that in the liquid phase. This means that adsorbate molecules are not able to occupy the zeolite channel space fully. In NaZSM-5 the sodium cations (0.97 Å ionic radius) are located inside the zeolite channels. These cations may cause steric hindrance to the molecules and prevent occupation of the pore volume completely. In the case of alkenes, there is a possibility of π-electrons of the olefin double bond to interact with sodium cations and thus reduce the mobility of the olefinic carbon chain as compared to the alkane molecule. This also will affect the closer packing of the molecules inside the channel and thus reduce the total amount adsorbed, as observed in this study.

The effect of the temperature on the adsorption saturation capacities for alkanes and alkenes (Tables 2 and 3) shows that these values decrease with an increase in temperature. Further, the decrease is more for alkanes than for alkenes. The decrease in adsorption with an increase in temperature is only to be expected because adsorption is an exothermic phenomenon and an increase in the adsorption temperature will result in a decrease in adsorption.

It has been reported (1, 2) that it is more informative to express the adsorption in terms of the effective total carbon chain length of the sorbate molecules per unit cell. This is calculated as the product of the carbon chain length of the sorbate molecule and the number of molecules adsorbed per unit cell. The carbon chain length of the various adsorbate molecules was calculated using the equation

$$\text{Length (Å)} = 5.26 + 1.26(n - 2) \tag{3}$$

where n is the carbon number of the molecule. The value 5.26 is the length of the ethane molecule. For all olefin molecules, 0.34 Å (the difference between C—C single bond and C—C double bond lengths) was deducted from the length of a normal alkane molecule.

The total channel length of the ZSM-5 zeolite is given in Table 4 where each unit cell is constructed from four segments of linear channel (4 × 4.6 Å), four segments of sinusoidal channel (4 × 6.6 Å), and four channel intersections (4 × 5.4 Å). These are also shown in Fig. 2. The number of molecules adsorbed per unit cell, assuming 1 or 2 molecules per intersection, is calculated from the total channel length of the unit cell. This is given in Table 5 along with the experimental saturation adsorption capacity expressed in terms of molecules per unit cell. By comparing the observed and the calculated effective channel lengths (Table 5), it is evident that the normal alkane and alkene molecules are arranged with 2 molecules per intersection at 10°C. At 30 and 50°C the packing is between 1 to 2 molecules per intersection.

Normal alkane and alkene molecules have a critical diameter of 4.8 Å, which is less than both the linear and sinusoidal channel diameters of ZSM-5. As a result, these can be adsorbed into both the channels. The

TABLE 4
Channel Lengths in ZSM-5

Channel type	Channel length (Å/unit cell)[a]
Sinusoidal channel and intersection only	48.3
Linear channel and intersections only	39.8
Sinusoidal and linear channels and intersection with one molecule per intersection	66.5
Sinusoidal and linear channels and intersection with two molecules per intersection	88.1

[a] Unit cell consists of:
Four segments of linear channel (4 × 4.6 Å)
Four segments of sinusoidal channel (4 × 6.6 Å)
Four channel intersections (4 × 5.4 Å)

adsorption of *n*-alkanes/alkenes is dominated by dispersion forces, and the adsorbate molecule will be preferentially located in the sites where its interaction with a zeolitic wall is greater. Hence, at low adsorbate loading the adsorbate molecules are located in the channel segments. However, as the carbon chain length increases, the molecules are also located within the intersection of the channels. This leads to enhanced

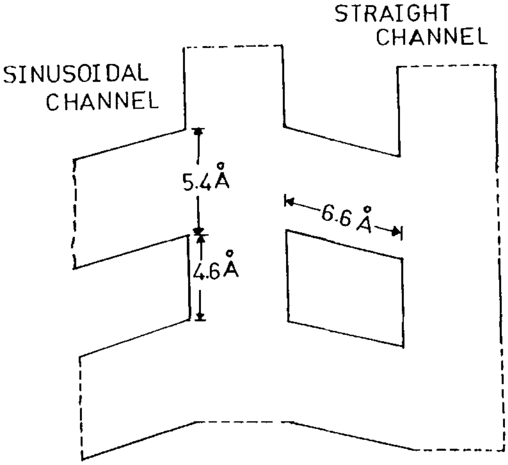

FIG. 2 Zeolite channel structure.

TABLE 5
Equilibrium Sorption Capacities of Alkanes and Alkenes in ZSM-5

		Equilibrium capacity (V_m) (molecular per unit cell)				
		Theoretical		Experimental		
Adsorbate	Adsorbate length (Å)	Two molecules per intersection	One molecule per intersection	10°C	30°C	50°C
n-Octane	12.82	6.8	5.2	6.3	5.7	5.5
n-Undecane	16.60	5.3	4.0	4.9	4.6	4.6
n-Dodecane	17.86	4.9	3.7	4.9	4.1	3.8
n-Tetradecane	20.38	4.3	3.3	4.2	4.1	3.6
n-Pentadecane	21.64	4.1	3.1	3.9	3.7	3.5
1-Octene	12.64	6.9	5.3	6.3	5.9	6.1
1-Undecene	16.42	5.4	4.1	4.6	4.5	4.4
1-Dodecene	17.68	5.0	3.8	4.4	4.3	4.2
1-Tetradecene	20.38	4.3	3.3	—	4.1	—

adsorbate–adsorbate interactions because only end methyl group can interact inside the channels whereas lateral interactions between adsorbate molecules are also possible inside the intersections. For the compounds studied in the present work, the length of the carbon chain is greater than that of the channel segment length. Hence, the adsorbate molecules always extend into the intersections. The packing arrangement predicted by Richards and Rees (2) within zeolite channels for molecules having a carbon chain length less than hexane can be extended to chain lengths greater than hexane. The increased adsorbate–adsorbate interactions are also reflected in the limited heats of adsorption data reported for *n*-hexane (2) and *n*-decane (1) in ZSM-5 and silicalite. The heat of adsorption, as expected, increases from its zero value to a maximum value in the vicinity of the saturation adsorption capacity value. It will be very interesting to observe the change in packing pattern with adsorbate coverage from lower to higher values.

Adsorption of Octane Isomers

The effect of methyl group substitution on the carbon chain on the adsorption properties of a molecule has been studied by measuring the adsorption of *n*-octane and its isomers having one, two, and three methyl groups. The saturation equilibrium adsorption capacities for these compounds are given in Table 6. The adsorption isotherms at 10, 30, and 50°C for the isomeric compounds (Fig. 3) were fitted into the Langmuir isotherm, and the experimental data are given in Table 1. For those isomers where no significant adsorption was observed, the data were not fitted and the saturation values were taken from the data as such.

From the adsorption capacity data given in Table 6, it can be noted that when a molecule has a single methyl group or two methyl groups on different carbon atoms (e.g., 4-methylheptane and 2,5-dimethylhexane), significant adsorption is observed. However, when the molecule has more than one methyl group on one carbon atom or three methyl groups attached to three different carbon atoms, the adsorption is negligible (e.g., 2,3,4-trimethylpentane and 2,2,4-trimethylpentane).

2,2,4-Trimethylpentane has a tertiary carbon atom with two methyl groups attached at the same carbon atom. This results in a larger molecular dimension (with 0.59 × 0.62 Å cross-sectional diameter) than the pore openings of the ZSM-5 zeolite channel. As a result, the molecules are

TABLE 6
Equilibrium Adsorption Capacity for Isomers of Octane in ZSM-5 at Different Temperatures

		Equilibrium capacity (V_m) (mmol·g^{-1})		
			Calculated	
Adsorbate[a]	T (°C)	Experimental	Density	Dubinin
n-Octane (12.82 × 3.9 × 4.3)				
	10	1.0840	1.1820	1.2499
	30	0.9856	1.1552	1.1671
	50	0.9451	1.1284	1.1324
2,5-Dimethylhexane (10.30 × 5.8 × 4.6)				
	10	0.6724	1.1662	0.7011
	30	0.8572	1.1395	0.6851
	50	0.7931	1.1144	0.6682
4-Methylheptane (11.56 × 5.8 × 4.6)				
	10	1.3118	1.1856	0.7128
	30	1.2189	1.1585	0.6965
	50	0.8642	1.1314	0.6802
2,3,4-Trimethylpentane (9.04 × 5.8 × 4.6)				
	10	—	1.1645	0.7001
	30	0.1390	1.1370	0.6836
	50	0.2211	1.1094	0.6670

[a] The data given in parentheses are the molecular dimensions in Å estimated by the space-filling model.

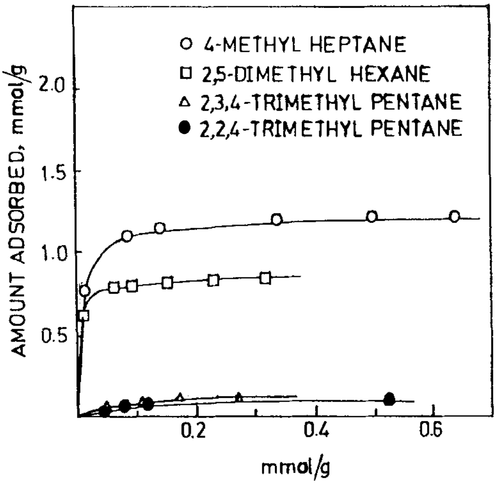

FIG. 3 Adsorption isotherms for octane isomers in ZSM-5.

unable to enter the zeolite channels and negligible adsorption is observed. In the cases of 4-methylheptane and 2,5-dimethylhexane the cross-sectional diameters are 0.48 × 0.56 Å, which are smaller than the ZSM-5 channel openings. Accordingly, a substantial adsorption is observed for these molecules. However, it is surprising that almost no adsorption is seen for 2,3,4-trimethylpentane as its cross-sectional diameter is not more than that of the channel entrance. This may be because of one or both of the following reasons:

1. Higher activation energy of diffusion (low adsorption rate of 2,3,4-trimethylpentane).
2. Packing inside the channel is not favorable toward adsorption of these molecules.

If the adsorption rate is low due to a high energy of activation, then increased adsorption should be observed at higher temperature, i.e., 30 and 50°C. As the molecule has three methyl groups substituted on the neighboring carbon atoms, the flexibility of the carbon chain is reduced. It is also difficult for such molecules to be adsorbed inside the channels of the zeolite. For example, for the 2,5-dimethylhexane molecule, two methyl groups are on the carbon atoms separated by two carbon atoms. Such a molecule may be adsorbed inside the channel in such a fashion that when methyl groups are located in the intersections, and carbon chain is inside the channel segment. Such a packing is also supported by the calculated values for molecules per unit cell which show that for 2,5-dimethylhexane the saturation capacity corresponds to 1 molecule per unit intersection compared to *n*-octane or 4-methylheptane where 2 molecules per intersection are present. For 2,3,4-trimethylpentane, the probability of three adjacent methyl groups in the intersection appears to be less because the carbon chain length supporting these groups is more than 5 Å. Since three methyl groups present in the same vicinity try to be away from each other because of repulsion, this moiety may effectively need more space than the amount of size available. Such a packing does not seem to be feasible inside the channels, and hence the adsorption of 2,3,4-trimethylpentane is not favored energetically.

Diffusion of Alkanes and Alkenes in ZSM-5

Sorption uptake curves for various compounds are shown in Fig. 4. The diffusion coefficients calculated (11) using Eq. (4) are given in Table 7 along with the data reported in the literature.

$$\frac{q_t - q_0}{q_\infty - q_0} = 1 - \frac{6}{\pi^2} \sum \frac{1}{n^2} \exp\left(\frac{-Dn^2\pi^2 t}{r^2}\right) \qquad (4)$$

where q_0, q_t, and q_∞ are the amounts adsorbed at times zero, t, and at equilibrium; D is the diffusivity coefficient.

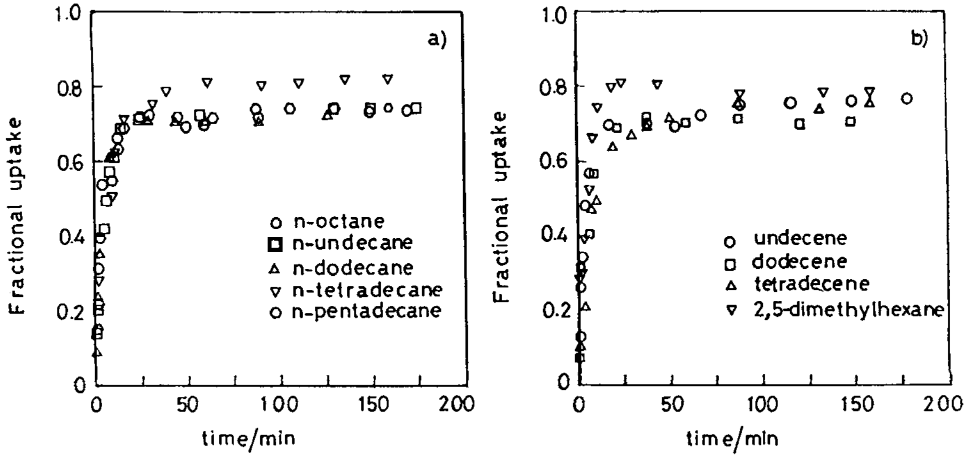

FIG. 4 Sorption uptake curves of (a) *n*-paraffins and (b) olefins and 2,5-dimethylhexane on ZSM-5 at 30°C

TABLE 7
Diffusivity Coefficient of Alkanes and Alkenes in NaZSM-5

Adsorbate	D (cm^2/s)	Temperature (°C)
Methane (5)	1.1×10^{-6}	61
Ethane (5)	2.2×10^{-7}	61
Propane (5)	7.3×10^{-8}	61
n-Butane (5)	7.3×10^{-8}	61
n-Pentane (5)	2.4×10^{-8}	61
n-Hexane (6)	1.3×10^{-11}	61
2,5-Dimethylhexane	7.5×10^{-12}	30
n-Octane	6.4×10^{-13}	30
n-Undecane	8.8×10^{-13}	30
n-Undecene	8.0×10^{-13}	30
n-Dodecane	8.0×10^{-13}	30
n-Dodecene	8.0×10^{-13}	30
n-Tetradecane	9.6×10^{-13}	30
n-Tetradecene	9.6×10^{-13}	30
n-Pentadecane	7.2×10^{-13}	30

It can be seen from the sorption uptake curves as well as the diffusion coefficient data that the adsorption kinetics does not vary significantly with the increase in carbon chain length for the compounds studied. Alkenes and alkanes also do not show significant differences in diffusion coefficients. The diffusion of these molecules is slow in ZSM-5 zeolite, showing intra-crystalline diffusivities of the order of 10^{-12}. Literature data were available only for lower hydrocarbons, and these were measured in the gas phase. However, the diffusion coefficients measured in the present study are in the liquid phase. Still, the effect of carbon chain length on the diffusion coefficient has been studied using these data. As seen from the data presented in Table 7, there is a sharp decrease in diffusion coefficient values as one goes from pentane to hexane. For example, the diffusion constant for normal pentane is of the order of 10^{-8} s^{-1} whereas it is 10^{-12} s^{-1} for the higher alkanes. Such a large decrease cannot be attributed to a shift from the gas to the liquid phase. This is an interesting observation because the carbon chain length of the alkane molecules matches the distance between the channel intersections of the straight channel (10 Å) for the hexane molecule which has a carbon chain length of 10.3 Å. Molecules larger than *n*-hexane may be adsorbing in such a manner that a segment of the molecule occupies the pore intersection. This molecular segment may obstruct molecular traffic along the zeolite channels and result in a sharp decrease in diffusion coefficients. Such a correlation between the carbon chain length of *n*-alkanes C_7 to C_{14} and the zeolite cavity size has been shown (12) for the zeolite NaCaA.

The effect of substitution of methyl groups on a carbon chain is seen by comparing the diffusion of 2,5-dimethylhexane with normal hexane (Table 7). The larger critical diameter of the former causes a significant decrease in the diffusion coefficient. A similar effect has been reported for butane and isobutane adsorption in ZSM-5 (11).

REFERENCES

1. P. A. Jacobs, H. K. Beyer and J. Valyon, *Zeolites*, *1*, 161 (1981).
2. R. E. Richards and L. V. C. Rees, *Langmuir*, *3*, 335 (1987).
3. Y. H. Ma, T. D. Tang, L. B. Sand, and L. Y. Hou, in *Studies in Surface Science and Catalysis*, Vol. 28 (Y. Murakami, A. Iijima, and J. W. Ward, Eds.), Kodaneva, Tokyo; Elsevier, Amsterdam, 1986, p. 531.
4. C. L. Cavalcante Jr. and D. M. Ruthven, *Ind. Eng. Chem. Res.*, *34*, 177, 185 (1995).
5. D. T. Hayhurst and A. R. Parvar, *Zeolites*, *8*, 27 (1988).
6. P. Wu, A. Debede, and Y. H. Ma, *Ibid.*, *3*, 118 (1983).
7. Y. H. Ma and Y. S. Lin, *AIChE Symp. Ser. 242*, *81*, 39 (1985).
8. N. V. Choudary, R. V. Jasra, S. G. T. Bhat, and T. S. R. Prasada Rao, in *Zeolites: Facts, Figures, Future* (P. A. Jacobs and R. A. van Santen, Eds.), Elsevier, Amsterdam, 1989, p. 867.
9. E. M. Flanigen, J. M. Bennet, R. W. Grose, J. P. Cohen, R. L. Patton, R. M. Kirchner, and J. V. Smith, *Nature*, *271*, 512 (1978).
10. M. M. Dubinin, *Chem. Rev.*, *60*, 235 (1960).
11. R. M. Barrer, *Zeolite and Clay Minerals as Sorbents and Molecular sieves*, Academic Press, New York, NY, 1978.
12. R. V. Jasra and S. G. T. Bhat, *Zeolites*, *7*, 127 (1987).

Received by editor June 5, 1996
Revision received October 1996