ADSORPTION AND DIFFUSION IN HZSM-5 ZEOLITE STUDIED BY AN OSCILLATING MICROBALANCE*

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A novel microbalance technique has been used to study diffusion and adsorption in a commercial HZSM-5 zeolite. This new technique uses an inertial microbalance TEOM (Tapered Element Oscillating Microbalance) to measure mass changes in the zeolite bed. Time resolution as short as 0.1 s, a flow-through design where all the probe molecules see the zeolite bed and high sensitivity allowing zeolite loadings down to a few milligrams are the three most important properties of the TEOM. The probe molecules studied were *o*-xylene, *p*-xylene and toluene which were introduced at 303, 373 or 473 K and at partial pressures in the range of 0.2–10 kPa. The inverse characteristic uptakes (D/L^2), corrected (D_0/L^2) and steady-state (D_{ss}/L^2) diffusion times are reported. The thermodynamic correction used for D_0/L^2 calculations almost eliminated the concentration dependence of the diffusivities. The D_{ss}/L^2 values were found to be rather unaffected by both temperature (373–473 K) and concentration, suggesting a certain degree of unification for diffusivities. *o*-Xylene uptake rates in the TEOM were found to be significantly higher than in a gravimetric microbalance under identical conditions, probably as a result of additional mass transfer resistance other than intracrystalline diffusion caused by poor contact between the gas phase and the zeolite in a conventional gravimetric microbalance.

Key words: Adsorption; Diffusion; Zeolites; Oscillating microbalance.

Zeolites are crystalline materials with well-defined pore systems extending in one, two or three dimensions. The medium pore size (10-ring) zeolite ZSM-5 exhibits shape selectivity and can convert linear and branched molecules, monocyclic aromatics, alicyclic and non-aromatics with critical molecular dimensions less than 0.6 nm. The shape selectivity occurs because the different-sized molecules travel through the inter-

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nal pore structure at different rates, and also due to total exclusion of bigger molecules. For the design of shape-selective catalytic conversion processes, it will be of great importance to be able to predict zeolite shape selectivity from the intracrystalline diffusivities.

During the past thirty years, much emphasis has been put on the development of reliable methods for studying intracrystalline diffusion in zeolites for a variety of probe molecules[1]. There appear to be large inconsistencies between reported zeolite diffusivities, often by several orders of magnitude. The discrepancies might occur in the definitions, interpretations, or translation of diffusivity values derived from, or applied to, different methods or experiments[2]. Different types of diffusivities, including intrinsic, non-steady-state and steady-state diffusivities have been defined and the relationships between the different diffusivities established. However, there are still large differences between reported data even for identical experimental methods using the same interpretation method[3].

The gravimetric method has been widely used for measuring diffusivities in zeolites due to its simplicity in experiments and interpretations[4–6]. A disadvantage with conventional gravimetric microbalances is the fact that a fraction of the probe molecules bypasses the sample basket, making it difficult to eliminate the additional resistances for mass and heat transport in the zeolite bed[7]. The effect of additional resistances to mass and heat transfer during diffusion measurements has been discussed by Kärger *et al.*[3]. The ZLC (Zero Length Column) was developed[8] to avoid these undesired effects. The new technique used in this work is based on a TEOM microbalance[9] (Tapered Element Oscillating Microbalance) where these problems are avoided. Originally developed for detecting particulates in the effluent of combustion systems[9], the TEOM microbalance has in recent years also been used to study catalytic conversion processes *in situ* coupled with deactivation such as catalytic cracking[10], methanol to olefins (MTO, ref.[11]) and ethene oligomerization[7]. The present work focuses on the study of adsorption and diffusion in HZSM-5 with this novel technique, taking advantage of the high mass resolution and the short response time which make this technique particularly suitable.

EXPERIMENTAL

The operation of the TEOM microbalance is based on Eq. (*1*) which is the relationship between the natural frequency of an oscillating quartz element which contains the zeolite sample, and its mass:

$$m_1 - m_0 = K_0 \left[\left(\frac{1}{f_1} \right)^2 - \left(\frac{1}{f_0} \right)^2 \right]. \tag{1}$$

K_0 is a calibration constant unique for each tapered element, m_1 and m_0 are masses corresponding to the frequencies f_1 and f_0. A Rupprecht & Patashnick TEOM 1500 Pulse Mass Analyzer (Albany, N.Y., U.S.A.) was used. The TEOM is equipped with a mechanical drive system which makes the tapered element oscillate at its natural frequency. Optics (transmitter and receiver) located on oppo-

site sides of the element perform the required frequency counting, which is related to the mass according to Eq. (*1*). Figure 1 illustrates the tapered element including the inlet and outlet for the probe molecules. The complete TEOM flow diagram was described earlier[7].

The zeolite used was a template-free ammonium form of the ZSM-5 zeolite (CBV 3020) with the unit cell formula of $Si_{90.51}Al_{5.48}O_{192}$ obtained from PQ Zeolites B.V. (PA, U.S.A.). The crystal sizes were ranging from 0.1–0.8 μm and the surface area was 430 m^2 g^{-1}. A zeolite loading of 7.6 mg (0.09–0.11 mm particles) was used. A lower loading resulted in a too low signal/noise ratio, whereas a higher loading was more likely to introduce concentration gradients in addition to a significant pressure drop over the zeolite bed. The zeolite was installed together with inert quartz particles (15 mg) between two layers of quartz wool. Helium was used as carrier gas, diluting agent and as purge gas. The zeolite was calcined *in situ* at 773 K for 12 h in dilute air containing 10% O_2.

After a stable weight signal was attained at the desired temperature, the probe molecules were introduced in the TEOM by switching between helium and helium saturated with the probe molecules in thermostated bottles at 303 K containing the probe molecules. A constant flow rate was always maintained through the microbalance. The saturation pressures at T = 303 K for the probe molecules used in this study[12] are shown in Table I together with literature values for their minimum molecular

TABLE I
Properties of the hydrocarbons used as probe molecules

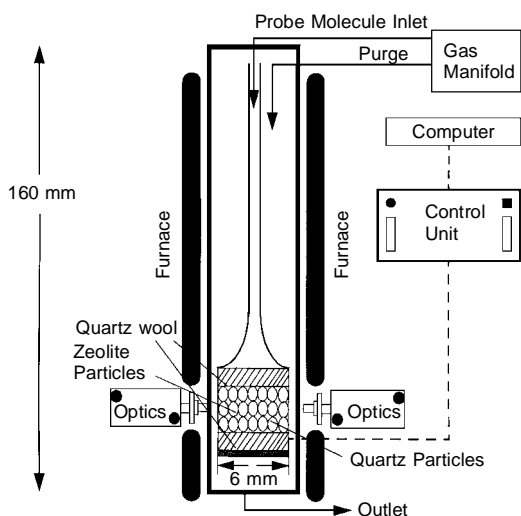| Compound	Saturation pressure at 303 K kPa (ref.[12])	Minimum molecular size nm (ref.[13])
Toluene	4.89	0.575
p-Xylene	1.55	0.575
o-Xylene	1.17	0.625

FIG. 1

Illustration of the principle for the Tapered Element Oscillating Microbalance (TEOM)

size[13]. Experiments were carried out at 303, 373 and 473 K and at partial pressures of the probe molecules in the range of 0.2–10 kPa. After each uptake curve, where the mass m_t and the time t were recorded, the zeolite was heated at 5 K min^{-1} up to 773 K in helium and kept at this temperature for 2 h. After cooling, the system was kept at the desired temperature until the weight curve had returned to the baseline (the value before adsorption). If there was a permanent weight change, the zeolite was regenerated in air at 823 K for 8 h. After the *o*-xylene experiments, the zeolite had to be regenerated in air.

Some adsorption experiments were also carried out in a conventional C. I. Electronics Mark 2B (Wiltshire, U.K.) microbalance for comparison. Details of the experimental setup for the conventional microbalance has been described elsewhere[14]. These experiments were carried out using 13.9 mg zeolite, and with the same partial pressures and temperatures as in the TEOM. The probe molecules were introduced through a three-way valve positioned close to the zeolite bed.

Interpretation of Experimental Data

It is recommended to operate with dilute systems and low zeolite loadings to prevent concentration gradients in the zeolite bed during diffusion measurements. For an isothermal system where the uptake rate is controlled by intracrystalline diffusion with only a small concentration gradient for the adsorbed phase (constant D), solutions of the transient diffusion equation for different geometries have been given[15]. Simplified and convenient solutions for short times (low m_t/m_∞) and long times (high m_t/m_∞) are available[3]. By comparing the intercept when $(1 - m_t/m_\infty)$ is plotted with time on stream for long times, the geometry that fits the uptake data best can be determined. The interception will be close to $8/\pi^2$ for a one-dimensional model corresponding to a slab geometry and close to $6/\pi^2$ for a three-dimensional spherical model[3]. For most of the systems studied in this work, the one-dimensional model for a slab geometry represented by Eq. (*2*) turned out to fit the experimental data best. L in Eq. (*2*) is the length of the diffusion path.

$$\frac{m_t}{m_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 \pi^2 D t}{4L^2}\right) \tag{2}$$

This model is expected to describe the case when diffusion occurs predominantly through the straight channels of HZSM-5. Figure 2 illustrates the consistency between the one-dimensional model and an experimental uptake curve for *p*-xylene at 473 K with a partial pressure *p* of 0.5 kPa obtained in the
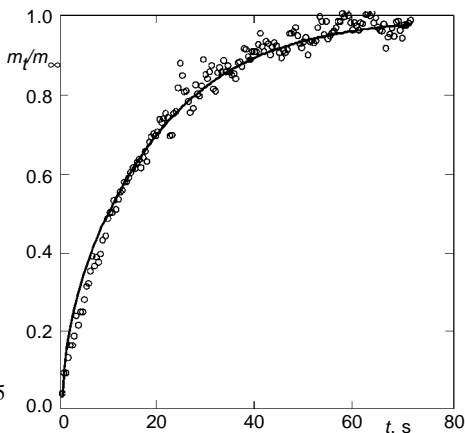

Fig. 2
Uptake curve for *p*-xylene at 473 K and *p* = 0.5 kPa fitted to Eq. (*2*) giving $D/L^2 = 0.0053$ s^{-1}

TEOM. Most reports in the literature treat diffusion in well defined large crystals, and the intracrystalline diffusivities are calculated by assuming an average crystal radius as the difussion path. Since L was uncertain in this study because of non-uniform crystal sizes, the inverse characteristic diffusion time D/L^2 is reported. When applied to catalytic reactions, the knowledge of the characteristic diffusion time L^2/D rather than D is important since the square of the Thiele modulus is directly proportional to the ratio of the characteristic diffusion time to the characteristic reaction time.

The corrected diffusivity (D_0) can be obtained from the uptake diffusivity D by the Darken equation[3]:

$$D_0 = D\left(\frac{\mathrm{d}\ln q}{\mathrm{d}\ln p}\right) . \tag{3}$$

Equation (3) has been widely used to describe the concentration dependence of the diffusivity measured in zeolite systems and is often interpreted as a phenomenological irreversible thermodynamic relation[16]. Equation (3) is based on the argument that the true driving force for diffusion is the gradient of the chemical potential rather than that of the concentration. At higher concentration levels, the adsorption isotherm becomes non-linear and the concentration gradient is no longer that of the chemical potential. When using this model, the isotherm of the system must be measured to obtain the relationship between the gas phase pressure (p) and the concentration in the zeolite (q). The type I isotherm in Brunauer's classification[17] for single probe molecules, described by the ideal Langmuir model, is such a relation:

$$\frac{1}{q} = \frac{1}{q_\mathrm{s}} + \left(\frac{1}{bq_\mathrm{s}}\right)\frac{1}{p} . \tag{4}$$

The uptake diffusivities D are obtained from transient experiments where diffusion is accompanied by adsorption in the zeolite. In order to obtain reactive diffusivities, where diffusion is followed by a reaction, the uptake (non-steady-state) should be transformed to steady-state conditions. The steady-state diffusivity D_ss at steady-state has been shown by Garcia and Weisz[2] to be:

$$D_\mathrm{ss} = \left(\frac{C_\mathrm{T\infty}}{C_0\beta}\right)D , \tag{5}$$

where $C_\mathrm{T\infty}$ is the total equilibrium amount of the probe molecules adsorbed at the gas phase concentration C_0. Equation (5) is valid when all the adsorbed molecules are equally mobile. β depends on the curvature of the adsorption isotherm, but this correction was found[2] to be of minor importance compared to the potentially very large correction factor $C_\mathrm{T\infty}/C_0$. β can therefore be assumed to be unity[2]. For linear isotherms, the relation between $C_\mathrm{T\infty}$ and C_0 is the Henry's law constant. Of the few studies trying to couple physical and catalytic measurements, the work of Post et al.[18] should be mentioned. They introduced Henry's law constant (measured at low temperatures) in the Thiele modulus and found consistency between diffusivities derived from uptake data and catalytic behaviour. Adsorption equilibrium, diffusion rates and the conversion of 2,2-dimethylbutane over ZSM-5 zeolites with various crystal sizes and aluminium contents were determined.

RESULTS AND DISCUSSION

The obtained uptake curves from exposure of HZSM-5 to probe molecules at $T = 303$, 373 or 473 K were fitted to Eq. (2) and solved for D/L^2. The saturation concentration in

the adsorbed phase (q_s) at different partial pressures was used to obtain the Langmuir adsorption isotherm, Eq. (*4*). The adsorption parameters are reported in Table II, and Figs 3–5 illustrate the adsorption isotherms for *p*-xylene, toluene and *o*-xylene, respectively, in the temperature range 303–473 K.

D_0/L^2 were calculated from D/L^2 by the Darken equation (Eq. (*3*)), when L was assumed constant. Figures 6 and 7 show D/L^2 and D_0/L^2 for *p*-xylene. D/L^2 displays the normally reported increase with concentration and depends largely on the temperature. The use of D_0/L^2 was found to almost eliminate the effect of external gas phase concentration, C_0. For the other probe molecules, only D_0/L^2 and D_{ss}/L^2 will be presented

TABLE II
Parameters of Langmuir model (Eq. (*4*)) for the adsorption of probe molecules at 303, 373 and 473 K on HZSM-5 zeolite

Compound	Temperature, K	q_s, $g_{ads}\,g_{zeol}^{-1}$	b, kPa^{-1}
Toluene	303	0.080	17.89
Toluene	373	0.058	9.95
Toluene	473	0.028	1.19
p-Xylene	303	0.105	15.37
p-Xylene	373	0.069	28.90
p-Xylene	473	0.036	3.98
o-Xylene	473	0.023	3.30

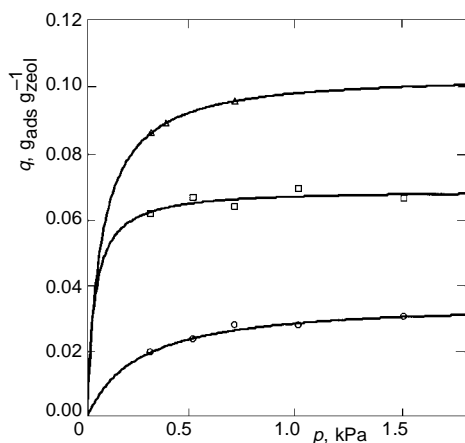FIG. 3
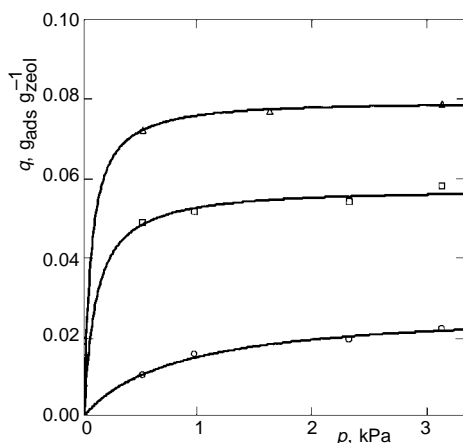*p*-Xylene equilibrium adsorption data fitted to the Langmuir model, Eq. (*4*), at 303 K (Δ), 373 K (□), and 473 K (○)

FIG. 4
Toluene equilibrium adsorption data fitted to the Langmuir model, Eq. (*4*), at 303 K (Δ), 373 K (□), and 473 K (○)

because they contain a certain degree of unification for temperature and/or concentration.

Table III gives D_0/L^2 for *o*-xylene at 473 K which shows a decreasing trend with partial pressure. No simple trend in the inverse characteristic corrected diffusion time with temperature was found at low temperatures. Values of D_0/L^2 at 303 K were larger than at 373 K for *p*-xylene (Fig. 7) while D_0/L^2 at both 303 K and 373 K were rather close for toluene (Fig. 8). This might be explained by a transition of diffusion to a different mechanism at low temperature, as proposed by Garcia and Weisz[2]. The phenomena capillary condensation, capillary flow or surface spreading will affect the diffusivity measurement and its interpretation at low temperatures. Equation (*2*) contains the inherent assumption that all molecules contribute equally to the process of stochastic displacement. This assumption does not seem to be valid at low temperatures, and Garcia and Weisz[2] found the conditions for irregularities in the dependence of initial sorption rate *versus* temperature.

D_{ss}/L^2 were calculated by Eq. (*5*) for different probe molecules and temperatures by assuming L to be constant; they are shown in Fig. 9. No values for D_{ss}/L^2 obtained at

TABLE III
D_0/L^2 for *o*-xylene at 473 K

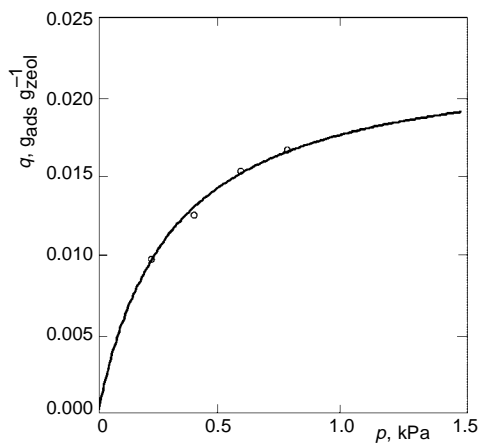| Partial pressure, kPa	0.2	0.4	0.6	0.8
$(D_0/L^2) \cdot 10^{-3}$, s^{-1}	1.5	1.1	1.0	0.8

FIG. 5
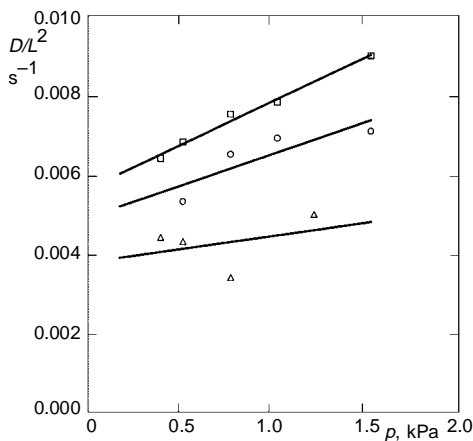*o*-Xylene equilibrium adsorption data fitted to the Langmuir model, Eq. (*4*), at 473 K

FIG. 6
D/L^2 for *p*-xylene at 303 K (Δ), 373 K ($\square$), and 473 K ($\bigcirc$)

303 K are plotted because of the transition region[2] at low temperatures described above. D_{ss}/L^2 seem to be rather constant with both concentration and temperature (373–473 K). A reason for the temperature uniformity has been indicated by Post *et al.*[18], who found that the activation energy for the diffusion (uptake) of 2,2-dimethylbutane in ZSM-5 was roughly equal to its heat of adsorption.

The ratios for D_{ss}/L^2 found in the present work were: 12 (toluene) : 8 (*p*-xylene) : 1 (*o*-xylene). This trend of the inverse characteristic diffusion time was found also for D/L^2 and D_0/L^2, and the lower value for *o*-xylene corresponds with a higher kinetic diameter of
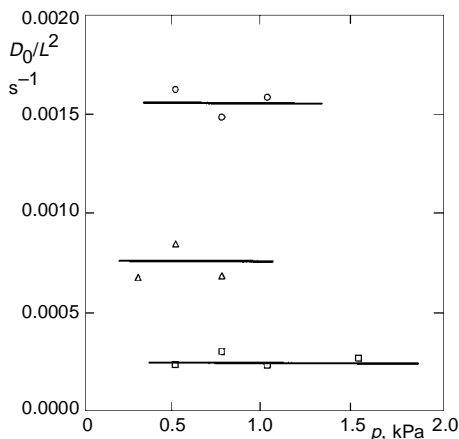

FIG. 7

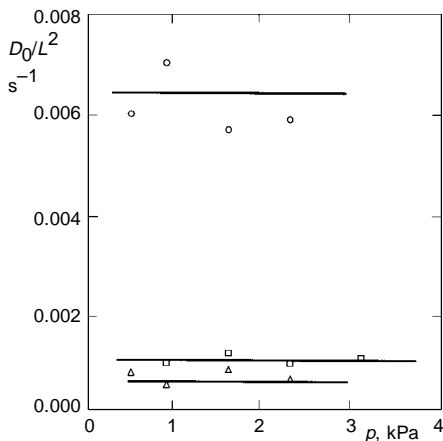D_0/L^2 for *p*-xylene at 303 K (Δ), 373 K (□), and 473 K (○)

FIG. 8

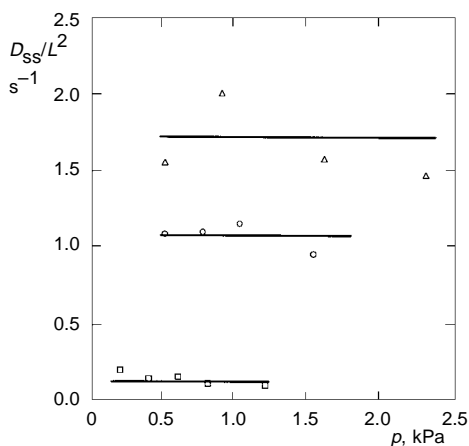D_0/L^2 for toluene at 303 K (Δ), 373 K (□), and 473 K (○)

FIG. 9

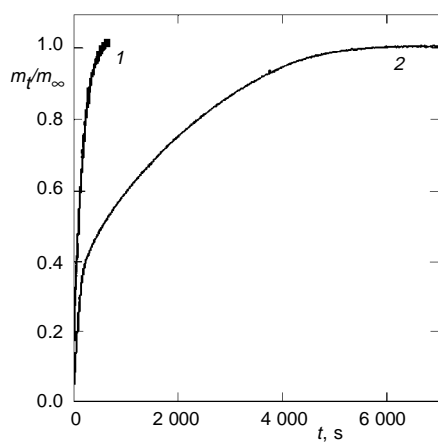D_{ss}/L^2 for *o*-xylene (□), *p*-xylene (○), and toluene (Δ)

FIG. 10

Uptake curves for *o*-xylene at 303 K in the TEOM (*1*) and the gravimetric microbalance (*2*)

this molecule according to Table I. The average crystal size obtained by SEM of the zeolite sample was about 0.5 μm, and by taking this as the diffusion path L, values for D, D_0 and D_{ss} can be obtained. Consistency between this study and other studies reviewed by Kärger and Ruthven[3] on diffusion in silicalite/ZSM-5 was observed. The present study gives uptake diffusivities D of $3 \cdot 10^{-15}\,\mathrm{m^2\,s^{-1}}$ for toluene, $1 \cdot 10^{-15}\,\mathrm{m^2\,s^{-1}}$ for p-xylene and $6 \cdot 10^{-16}\,\mathrm{m^2\,s^{-1}}$ for o-xylene at 303 K and at partial pressures less than 0.5 kPa.

Figure 10 compares the uptake curves at $T = 303$ K and an o-xylene partial pressure of $p = 1.2$ kPa obtained from the TEOM and from the conventional gravimetric microbalance. The catalyst mass was 7.2 mg in the TEOM, while the catalyst mass in the conventional microbalance was 13.9 mg (lowest possible loading due to the signal/noise ratio). The maximum amount adsorbed (q_s) in the TEOM and the gravimetric microbalance corresponded well. However, it can easily be seen from Fig. 10 that the time to reach equilibrium is much longer in the gravimetric microbalance than for the TEOM, probably due to additional mass transfer resistance in the catalyst basket. The mechanism for transport through the zeolite in the basket of the conventional microbalance was discussed previously[19], and proposed to occur by molecular diffusion and very little by convective flow. The mass and temperature gradients in the bed will depend on the height of the sample bed, *i.e.* sample loading, which is in agreement with the results obtained by Kärger *et al.*[3]. This clearly shows one of the advantages of TEOM for diffusion measurements: the removal of additional heat and mass transfer resistance by using low zeolite loadings and high flow rates through the sample. This is similar to the Zero Length Column, but the experiments and interpretation of experimental data are more simple in the TEOM.

CONCLUSIONS

Adsorption and diffusion experiments with o-xylene, p-xylene and toluene in HZSM-5 have been carried out at different partial pressures and temperatures in an oscillating microbalance (TEOM). D_0/L^2 eliminated to a large extent the concentration dependence and D_{ss}/L^2 were found to be almost constant with both concentration and temperature (373–473 K) for the probe molecules studied. The following trend was found for D_{ss}/L^2:

D_{ss}/L^2 (toluene) > D_{ss}/L^2 (p-xylene) > D_{ss}/L^2 (o-xylene),

the ratios being 12 : 8 : 1, respectively. An estimate of D, D_0 and D_{ss} could be obtained by assuming an average crystal radius; the values found were reasonable when compared with literature values. Comparison between results for o-xylene adsorption in a conventional gravimetric microbalance and the TEOM showed that the rate of uptake was significantly lower in the gravimetric microbalance, which is explained by additional mass transfer resistance in the zeolite bed.

SYMBOLS

β	correction factor
b	Langmuir constant , kPa^{-1}
C_0	concentration of the probe molecules in the gas phase, $mol\ m^{-3}$
$C_{T\infty}$	total equilibrium amount adsorbed at the gas phase concentration C_0, $mol\ m^{-3}$
D	uptake diffusivity, $cm^2\ s^{-1}$
D_0	corrected diffusivity, $cm^2\ s^{-1}$
D_{ss}	steady-state diffusivity, $cm^2\ s^{-1}$
f_1, f_0	natural oscillating frequencies at different sampling times, s^{-1}
K_0	the spring (tapered element) constant, $kg\ s^{-2}$
L	crystal half-thickness (one-dimensional model), cm
m_t	mass adsorbed at time t, g
m_∞	mass adsorbed at time t_∞, g
m_1, m_0	mass corresponding with frequencies f_1 and f_0, g
p	partial pressure of probe molecule, kPa
q	adsorbed phase concentration, $g_{ads}\ g_{zeol}^{-1}$
q_s	saturation concentration in adsorbed phase, $g_{ads}\ g_{zeol}^{-1}$
t	time, s

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