Adsorption and Diffusion in Microporous Materials

An Experimental Study with the TEOM

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Propositions of the doctoral dissertation entitled

**Adsorption and Diffusion in Microporous Materials:**
An Experimental Study with the TEOM

by Weidong Zhu

1. The commonly used collision diameters or Lennard-Jones potential constants\(^1\) are improper for determining the accessibility of molecules to channels and/or apertures in microporous materials. The shape-selective adsorption of propene over propane in DD3R supports the above concept.\(^2\)
   2) Chapter 6 of this thesis.

2. Bülow and Micke's claim that the intracrystalline diffusivity of \(n\)-hexane in silicalite-1, derived from the uptake rate determined by the piezometric method, confirms spectroscopic self-diffusivity data is questionable.

3. The thermodynamic (correction) factor plays an important role in the determination of concentration-dependent diffusivities in zeolite crystals and other microporous solids.
   *Chapter 5 of this thesis.*

4. The observed two-step adsorption behavior for single-branched alkanes in silicalite-1 is attributed to the large difference in the adsorption entropy between the molecular locations in the intersections and in the channels.
   *Chapters 3 and 4 of this thesis.*

5. Zeolite-based Fischer-Tropsch catalysts are inapplicable to the production of diesel fuels on an industrial scale.

6. Chang and co-workers' concept that a membrane reactor offers benefits to minimize catalyst deactivation by selective removal of HCl is incorrect. The catalyst deactivation during the hydrodechlorination of 1,2-dichloroethane is mainly ascribed to coke deposition rather than interactions between HCl and catalyst.

7. Molecular simulations become increasingly important in Chemistry and stimulate the transition from "Chemistry is Physics without thought" to "Chemistry is Physics with thought".

8. The all-silica DD3R is applicable to the kinetic separation of smaller molecules.
9. The “activation energy” barrier for the public to understand *Science* is still too high to be easily overcome. The resolution that scientists explain Einstein’s theory of *Relativity* into popular songs remains a challenge for the future.

10. The reputations of scientists are often derived from their publications and/or citation rates. But the publications and/or citation rates can only reflect their scientific reputations.

11. During the cultural revolution in the period 1966-1976, Chinese pupils were obliged to study Chairman Mao’s quotations, one kind of *philosophy*. However, few of them could become Doctors of *Philosophy* after growing up.

12. The USA government is still exaggerating the difference between *Capitalism* and *Socialism*. But this difference becomes negligible for most Chinese people.
Stellingen behorende bij het proefschrift:

**Adsorptie en Diffusie in Microporeuze Materialen: Een Experimentele Studie met de TEOM**

door Weidong Zhu

1. De veel gebruikte botsingsdiameters of Lennard-Jones potentiendalest is voor de bepaling van de toegankelijkheid van kanalen en/of openingen in microporeuze materialen ongeschikt. Dit blijkt uit de vormselectieve adsorptie van propeen ten opzichte van propaan in DD3R.

   2) Hoofdstuk 6 van dit proefschrift.

2. Bülow en Micke hebben de interkristallijn diffusiecoëfficiënt van hexaan in silicaliet-1 afgeleid van de opnamesnelheid bepaald met de piezometrische methode. Hun bewering dat deze waarde van de diffusiecoëfficiënt de zelfdiffusie gemeten middels spectroscopische technieken bevestigt, is twijfelachtig.


3. De thermodynamische correctiefactor speelt een belangrijke rol in de bepaling van concentratie-afhankelijke diffusiecoëfficiënten in zeolietkristallen en andere microporeuze materialen.

   *Hoofdstuk 5 van dit proefschrift.*

4. Het geobserveerde twee-staps adsorptiegedrag van enkelvertakte alkanen in silicaliet-1 kan worden toegeschreven aan het grote verschil in adsorptie-entropie tussen de adsorptieplaatsen in de kruisingen en in de kanalen.

   *Hoofdstuk 3 en 4 van dit proefschrift.*

5. De op zeolieten gebaseerde Fischer-Tropsch katalysatoren zijn niet geschikt voor de productie van dieselbrandstof op een industriële schaal.

6. De bewering van Chang et al. dat een membraanreactor katalysatordeactivering minimaliseert door de selectieve verwijdering van HCl, is niet correct. De katalysatordeactivering tijdens de hydrodechlorering van 1,2-dichloorethaan is vooral te wijten aan de afzetting van coke in plaats van de interactie tussen HCl en katalysator.


7. Moleculaire simulaties worden steeds belangrijker in de chemie en vormen de overgang tussen *Chemistry is Physics without thought* naar *Chemistry is Physics with thought*.
8. Silica DD3R is geschikt voor de kinetische scheiding van kleinere moleculen.

9. De "activeringsenergie" van het grote publiek voor het begrijpen van het blad *Science* is nog steeds te hoog. Het voornemen om de relativiteitstheorie van Einstein uit te leggen in popsongs blijft een uitdaging voor de toekomst.

10. De reputatie van wetenschappers is vaak gebaseerd op het betreffende aantal publicaties en/of citaties. Hierbij moet wel in het oog gehouden worden dat het aantal publicaties en/of citaties alleen iets zegt over hun *wetenschappelijke* reputatie.


12. De regering van de Verenigde Staten overdrijft het verschil tussen kapitalisme en socialisme. Voor een aanzienlijk deel van de wereldbevolking - de meeste Chinezen - is dit verschil echter verwaarloosbaar geworden.
Adsorption and Diffusion in Microporous Materials:
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Proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft
op gezag van de Rector Magnificus prof. ir. K.F. Wakker,
voorzitter van het College voor Promoties,
in het openbaar te verdedigen op dinsdag 8 mei 2001 om 10.30 uur

doors

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geboren te Zhejiang, China
This research was one of the projects in “Mastering the Molecules in Manufacturing”, abbreviated as M3, approved by the university board of Delft University of Technology.
Dedicated to

Zhangfeng & Feibai

"You do not really understand something unless you can explain it to your grandmother"

Albert Einstein
Microporous materials science is still expanding, and resulting in the discovery of synthetic materials with new topologies and new catalytic, adsorption and separation properties. The catalysis of microporous materials such as zeolites continues to be an area of particular interest with classic hydrocarbon conversions, oxidation reactions, formation of a greater variety of organic compounds, and environmental catalysis. Interest in adsorption and diffusion is very much revived and stimulated by the improvement of classic and the introduction of novel techniques for investigation. Other areas of interesting attractiveness are molecular modeling and theoretical developments.

Adsorption and diffusion phenomena are of scientific interest and widely used in practical applications. Microporous materials can selectively adsorb molecules based on a difference in molecular size and shape. Furthermore, separation processes using molecular sieves have a low-energy consumption as compared to, for example, distillation processes. For a proper design of adsorption-based separation or purification processes, accurate equilibrium data and diffusivities are important. In addition, accurate isotherm data and diffusivities for investigations in catalytic kinetics are of prime concern. The common techniques, i.e. volumetric and gravimetric methods, have been dramatically improved and developed in the system sensitivity, operating range, and automation over the past several decades. However, some drawbacks, especially for dynamic measurements, have not been solved due to the limitations of their operating principles. In this thesis, one of the objectives is to develop and evaluate a novel technique, the tapered element oscillating microbalance (TEOM), as applied to measurements of adsorption and diffusion properties of microporous materials.

Since July 1997 this Ph.D. research has been carried out at the Faculty of Applied Sciences, Delft University of Technology within the framework of the research programme “Model-Based Transient Processing in Heterogeneous Catalysis for Optimized Selectivity: Application to Fischer-Tropsch Synthesis”, which is one of the research projects in “Mastering the Molecules in Manufacturing”, abbreviated as M3. The focus was on the further development of Fischer-Tropsch synthesis, both catalyst improvement and optimized processing. Heterogeneous catalysis has long been more an art than science; in particular this is the case in catalyst design. For future breakthrough it is essential to develop fundamental models not only with respect to reactants, products, and transition states, but also with respect to sites and the local physical environment. The application of zeolitic-based catalysts is a new direction. A thorough understanding of the adsorption and diffusion of hydrocarbons in these microporous materials is a prerequisite for the interpretation of the kinetics of the reactions where these catalysts are employed. The latter is part of a complementary study. Therefore, the present activities were focused on the TEOM technique for catalyst characterizations and adsorption studies in the group of Industrial Catalysis, DelftChemTech, Delft University of Technology.
Since adsorption studies are most amenable to molecular modeling, the TEOM technique is a good starting point for these computational activities, which are considered to be main tools in the M3-research programme. In addition, adsorption and diffusion processes are main steps in catalytic reactions. These studies are beneficial for the understanding of catalytic kinetics and catalyst developments as well as for the separations of the desired products from mixtures. The work described in this thesis is related with the subject “Adsorption and Diffusion in Microporous Materials”.

Outline of the thesis

Chapter 1 gives a brief review on the volumetric and gravimetric techniques, as applied to measurements of adsorption data. Subsequently, a detailed description of the TEOM technique, including its operating principles and experimental procedures, is given.

Chapters 2 and 3 deal with the equilibrium adsorption of light alkanes in silicalite-1. A comprehensive comparison with literature data is made to confirm the validation of the TEOM technique. A dual-site Langmuir model is proposed to interpret the adsorption.

Equilibrium adsorption and diffusion of linear and branched C₆ alkanes in silicalite-1 crystals are studied in chapters 4 and 5. A detailed mathematical modeling is given to describe transient behaviors in the TEOM. An evaluation is made on the determination of intracrystalline diffusivities with the TEOM technique.

Shape selectivity in adsorption on the all-silica DD3R is presented in chapter 6. Theoretical considerations are made to interpret experimental results. Further discussions are conducted on the potential applications of the DD3R to the challenging industrial processes for propane and propene separations.

In the last chapter the main conclusions obtained in this research are summarized. The potential separations of linear and branched alkanes by silicalite-1 adsorbents and membranes and of propane/propene by the all-silica DD3R are evaluated. Furthermore, potential applications of the TEOM technique are discussed.

Weidong Zhu                                       Delft, January 2001

Each chapter in this thesis is written, based on separate publications, and can be read independently. Consequently, some overlap among the chapters is unavoidable.
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Adsorption Measurements: Techniques, Status, and Problems

The most common techniques for adsorption measurements, i.e. volumetric and gravimetric methods, have been briefly reviewed. For volumetric equipment measurements exhibit an accumulation of the errors. Data obtained by the gravimetric method are influenced by effects associated with flow patterns, bypassing, and aerodynamic factors such as buoyancy, resulting in extensive corrections. In addition, both techniques are not suitable for determining diffusivities in microporous materials, since external mass and heat transfer limitations are suspected to disguise the results.

The tapered element oscillating microbalance (TEOM), including its operating principles and experimental procedures, has been described in detail. Well-defined gas-solid phase conditions can be established in the TEOM due to a high flow rate of adsorptive and/or reactant gas in carrier gas through the sample bed without affecting measurements. This, in principle, can significantly improve external mass and heat transfer issues for microporous materials. In addition, experimental conditions in the TEOM can approach those of practical relevance to temperature, pressure, and flow. Therefore, the TEOM technique can circumvent most of the problems associated with either the volumetric or the gravimetric methods.
1.1 Introduction

The gas or vapor adsorption phenomenon is widely used in the field of gas separation and gas purification. It is also used in the characterization of porous solids. Each of these applications requires basic adsorption data in a particular range of experimental conditions (temperature, pressure, gas or vapor composition). These data consist of adsorption isotherms, selectivity curves, heats of adsorption or kinetic data.

In all adsorption measurements the first step is to obtain the surface of the adsorbent in the highest possible state of purity, i.e., to free it as completely as possible from gases already adsorbed before the beginning of the experiment. Theoretically, it should be possible to desorb all the Van der Waals' adsorbed gases merely by pumping, but in practice, particularly with adsorbents containing small pores, raising the temperature conveniently accelerates the process. An empirical equation derived by Orr and Dalla Valle\(^1\) offers a rough guide to suitable temperatures and times of outgassing. The time of heating, in hours, required to give reproducible surface areas by the gas adsorption method was given by

\[
 t = 1.44 \times 10^4 (T - 273.15)^{1.77}
\]

where \( T \) is the temperature of heating in Kelvin. Equation (1-1) applies to temperatures between 373.15 and 673.15 K and serves the system vacuum better than \( 6.7 \times 10^{-4} \) Pa.

With many solids the preparation of reproducible surface areas is complicated by the presence of an underlying layer of chemisorbed gases, often held so tenaciously that they cannot be removed without permanent damage (e.g. sintering, melting, etc.) to the surface. If the chemisorbed layer cannot be entirely removed, the outgassing treatment must be designed so that the surface is brought to the same condition prior to each experiment. In such a case, too vigorous outgassing might result in the removal of progressively small amounts of the chemisorbed gases during each outgassing process and so cause a gradual change in the adsorption properties of the solid with time. The outgassing processes are mentioned here since they are important for measuring accurate adsorption data. However, the detailed outgassing methods will not be discussed in this chapter.

In the study of adsorption and/or desorption rates and adsorption equilibria the quantity of gas or vapor adsorbed is always measured. In rate measurements the amount adsorbed is a function of time, in equilibrium measurements it is a function of the pressure or temperature. The determination may be direct or indirect. It is direct when either the volume or the weight of the amount adsorbed is measured, indirect when the measurement is made on some other physical properties of the adsorbed phase that have known functions related to the amount adsorbed.

This chapter presents an outline of the techniques employed in the measurement of adsorption of gaseous adsorptives by solids, paying special attention to the variety of methods that have been developed. It is not intended to write a comprehensive review of experimental apparatuses but to present the common principles to all methods of measurement and a few examples.
The two principal methods of measuring adsorption equilibria are classified as volumetric (barometric) and gravimetric, depending on whether the amount adsorbed is determined by means of experimentally measured pressures and gas-law relationships of the gas phase, or by direct measurement of the weight gained by the adsorbent.

As a major issue in this chapter, a novel technique, the so-called tapered element oscillating microbalance (TEOM in abbreviation), is introduced in detail. The current and potential applications of the TEOM technique to adsorption, diffusion, reaction, and catalyst deactivation are discussed.

Furthermore, a comprehensive comparison of various adsorption techniques is made to gain their advantages and drawbacks.

1.2 Volumetric Method

1.2.1 Principles
It is convenient to group together methods, in which the number of moles of gas or vapor adsorbed is calculated from accurate measurements of pressure, volume, and temperature. The principle underlying these methods is as follows. The pressure, volume, and temperature of a quantity of adsorptive are measured and the number of moles present calculated. The adsorbent material is then brought into contact with the adsorptive and, when constant pressure, volume, and temperature readings show the system to have attained equilibrium, the number of moles present in the gas phase is again calculated. The difference between the number of moles present initially and finally represents adsorptive 'lost' from the gas phase to the adsorbed phase.

The most common in the volumetric technique is to measure the changes in terms of adsorptive volume before and after adsorption. The measurement of adsorption is, therefore, equivalent to the gasometric determination of the apparent volume and the geometrical volume of a sample bulb. When the gas is ideal, the apparent volume \( V_{\text{app}} \) is defined as

\[
V_{\text{app}} = \frac{nR_g T}{p}
\]

where \( n \) is the total number of moles of adsorptive in the sample bulb and \( p, T, \) and \( R_g \) have their usual significance. The geometrical volume of the sample bulb, \( V_{\text{geo}} \), is given by

\[
V_{\text{geo}} = \frac{n_g R_g T}{p}
\]

where \( n_g \) is the number of moles of adsorptive in the gas phase side the sample bulb. The amount adsorbed is, therefore, \( n - n_g \), which is often expressed as \( V_{\text{app}} - V_{\text{geo}} \), corrected to standard conditions (STP) per gram of adsorbent.
The evaluation of the amount adsorbed is determined from pressure measurements in an apparatus of the type shown diagrammatically in Figure 1-1, which consists, *inter alia*, of a thermostatted sample bulb of volume $V_{geo}$ at temperature $T$, a container of accurately known volume $V_c$, and a pressure meter (barometer). The volume of the apparatus between stopcocks 1, 2, 3 and the pressure meter is $V_1$ at ambient temperature $T_a$; the volume between stopcock 3 and the thermostat bath is $V_2$, also at temperature $T_a$. These unknown volumes are determined as follows. Gas from the reservoir is introduced into the volume $V_1$ of the previously evacuated system and the resulting pressure $p_1$ is measured; stopcock 2 is then opened, the gas expands into $V_c$ to a pressure $p_2$; then at constant temperature, $V_1$ can be calculated by eqn. (1-4).

$$V_1 = V_c \frac{p_2}{p_1 - p_2}$$  

(1-4)

Finally, the gas at a measured pressure may be expended from $V_1$ into the sample-side of the system by opening stopcock 3. The volume of the sample-side, calculated from the results of this operation, is called the ‘dead-space’, it is not, however, the actual volume of the sample-side unless the thermostat bath is at ambient temperature. The volume of the dead-space, $V_d$, is given by

$$V_d = V_2 + \frac{V_{geo} T_a}{T}$$  

(1-5)

These volumes of the system, $V_1$ and $V_d$, must be measured with the adsorbent present inside the sample bulb; the gas used must not be measurably adsorbed at the temperature $T$, helium being the most suitable gas. Sometimes other gases, like argon, nitrogen, etc., are used at temperatures, at which their adsorption is likely to be negligible.

For the determination of an adsorption isotherm the volume $V_c$ is not used; adsorptive gas or vapor is introduced into $V_1$ from the reservoir and the amount of the dose calculated as a volume change at the standard temperature and pressure (SPT) by the relation

$$\Delta V_{dose} = \frac{T_0}{T} \frac{\Delta p_{dose}}{p_0} V_1$$  

(1-6)

where $\Delta p_{dose}$ is the increase of pressure in $V_1$, $T_0$ is the standard temperature of 273.15 K, and $p_0$ is the standard pressure of $1.013 \times 10^5$ Pa. Next, stopcock 3 is opened and the gas is allowed to equilibrate with the sample. When the equilibrium is reached, the amount of gas not adsorbed is calculated by eqn. (1-7)

$$V_{unads} = \frac{T_0}{T} \frac{p}{p_0} (V_1 + V_d)$$  

(1-7)
where $p$ is the equilibrium pressure. The specific amount adsorbed, expressed as the adsorptive volume at STP per gram of adsorbent, is calculated by

$$V = \frac{\sum \Delta V_{\text{dose}} - V_{\text{unads}}}{W}$$

(1-8)

where $\sum \Delta V_{\text{dose}}$ is the total amount of adsorptive in the system and $W$ is the mass of the adsorbent. Successive points on the isotherm are determined by admitting another dose and so reaching another equilibrium pressure. The adsorption isotherm thus determined is reported graphically by plotting $V$ versus $p$.

In practice it is convenient either to fix the volume and temperature and measure changes in pressure, or to keep the temperature and pressure constant and measure the diminution in volume. Since the latter involves the continuous adjustment of mercury or oil levels in a barometer to keep the pressure constant as the system approaches equilibrium, it is best suited to the measurement of rates of adsorption, where results at constant pressure are more amenable to theoretical treatment.\(^2\) For equilibrium studies, however, the time-honored constant volume method is to be preferred. Since each range of relative pressures poses special technical problems and has its peculiar sources of error, the wide variety of arrangements for measuring adsorption at constant volume may best be classified according to the pressure ranges for which they are intended.

### 1.2.2 Possible errors

The calculations given in the previous section were based on the ideal gas law. It may well happen, however, that, in the range of pressures and temperatures used during investigations, the gas phase deviates significantly from ideality. A correction factor should be taken account of the deviation of the gas from the ideal gas law.

Another type of correction is required when a pressure reading is obtained from a barometer that is at a different temperature from that of the sample. The gas tends to pass from the cooler to the warmer region, and a steady state is reached when the pressure difference between the two regions is sufficient to balance this thermal effusion or transpiration.\(^3\) In the determination of an adsorption isotherm, thermal transpiration results in the measured equilibrium pressure being greater or less than the true value, accordingly as the temperature of the sample is lower or higher than the temperature of the barometer. The magnitude of the absolute and relative errors as a function of pressure has been reported that the error is significant at low pressures.\(^4\)

When the mean free path of the gas molecules is very much greater than the diameter of the connecting tube that is subject to the temperature gradient, the following relation holds:\(^4\)

$$\frac{p_1}{p_2} = \left(\frac{T_1}{T_2}\right)^{\frac{1}{2}}$$

(1-9)

where $p_1$ is the true equilibrium pressure over the sample at temperature $T_1$ and $p_2$ the pressure measured by the gauge at temperature $T_2$. Thus, for example, if a pressure gauge is at room temperature, e.g., 298 K, and the system under investigation is at liquid nitrogen temperature
(77 K), then \( p_1/p_2 \approx 0.50 \), which would lead to 100% error unless correction is made for this effect.

The glass tubing used to construct adsorption apparatus has usually an inside diameter of several millimeters to allow rapid diffusion of gas and short pump-out times; consequently, the pressure range of many adsorption measurements lies beyond the scope of eqn. (1-9), while still in the range where thermal transpiration causes significant errors.

A strictly theoretical correction for the effect of thermal transpiration can be obtained only for two extreme cases: (a) the mean free path is large compared to the diameter of the connecting tube, when eqn. (1-9) is applicable; and (b) the mean free path is very much smaller than the diameter of the tube, i.e. when Poiseuille’s law holds, there will be equality of pressure throughout the apparatus. The region between these two limiting cases is one of great difficulty from a theoretical point of view. The correction factor is indeed a complex function of the temperature, pressure, nature of the gas and material of the tubing. All efforts to describe the intermediate region of pressure are empirical in their final expression.

The errors of practice begin with possible errors in the calibration of the volumes of the apparatus. The accurate determination of the number of moles unadsorbed at equilibrium depends on a precise knowledge of the dead-space or space surrounding the adsorbent particles. Estimation of the quantity of unadsorbed gas is often complicated by the fact that part of the dead-space is at room temperature, part at the temperature of the adsorbent thermostat.

Since the amount adsorbed represents the difference between the amount admitted to the dead-space and the amount remaining there at equilibrium, it can only be evaluated with confidence if these two quantities are of unlike magnitude. The most favorable situation obtains under conditions, e.g. at low relative pressures, where virtually all the gas admitted is adsorbed and the amount unadsorbed is either negligible or represents only a minor correction term. As the relative pressure increases, the adsorption isotherm usually flattens out and the addition of further increments of gas does not bring about much increase in the amount adsorbed. Consequently, the amount unadsorbed becomes commensurate with the total amount of gas admitted. It is for this reason that the method is much less sensitive at a higher relative pressure, particularly with adsorbents having low surface/volume ratios, i.e. low specific surfaces. In order to overcome this decline in sensitivity at higher pressures, it is desirable to design the apparatus so as to minimize the dead-space volume.

The other concern about the accuracy of the dead space determination is the calibrating gas being used. It has been reported that some detectable amount of helium can be adsorbed by different solids such as charcoal and metal oxides at low temperatures. Since in most adsorption apparatus part of the dead-space is at room temperature and part of it in a constant temperature bath, one must determine the dead-space at least at two different temperatures to obtain the volumes of the two parts separately. Not only too low but also too high temperatures must be avoided, because at higher temperatures some errors may be introduced by the solubility of helium in glass.
1.3 Gravimetric Method

Gravimetric measurement is probably the oldest method of obtaining quantitative information in chemistry. It is the basis of the analysis, upon which other methods rely. Yet, except for some notable exceptions, its techniques have remained relatively unsophisticated, while other methods have undergone elaborate development.\(^7\)

By the gravimetric method the amount adsorbed is weighed using a vacuum microbalance; the equilibrium pressure is separately measured, i.e., the two measurements are independent of each other, unlike the volumetric method where the measurement of the equilibrium pressure is also used for the calculation of the amount adsorbed. The necessity of measuring doses of gas into the system is eliminated and, therefore, there is less chance of cumulative errors in the results.

Vacuum microbalances for adsorption measurements have been classified by Rhodin\(^8\) as follows: a) cantilever type; b) knife-edge type; c) torsion type; and d) spring type. These basic designs have been illustrated and discussed by Rhodin in terms of their total, sensibility, ease of fabrication, installation, calibration, and adsorption. Many of the articles referred to the vacuum microbalance techniques as applied to adsorption measurements are reviews or semi-

![Diagram](image)

1: Gas supply system; 2: microbalance; 3: vacuum pump; 4: thermostat; 5: adsorption chamber

Figure 1-2 Schematic diagram of gravimetric system.

reviews. The great bulk of the published work has appeared as the proceedings of the various vacuum microbalance conferences. These have been published as a series of volumes under the general title *Vacuum Microbalance Techniques*. In this section the emphasis will be on the growing awareness of problems arising from buoyancy with the accuracy of the gravimetric method.

In summary, a gravimetric adsorption system requires four major components: 1) a sensitive balance to measure the change in the sample mass; 2) a pressure transducer to monitor the pressure of the sample chamber; 3) a vacuum station to evacuate and outgas the system; and 4) a suitable adsorptive reservoir. In addition to these major components, some additional devices are needed to complete the system, such as a constant temperature bath to
maintain the sample at a fixed temperature; a valve arrangement to expose the adsorption chamber to adsorptive or vacuum; and a method to follow both weight and pressure changes.

Here a symmetric-gravimetric microbalance is being considered. The sample side is designated as "I" and the reference side is designated as "II", as schematically shown in Figure 1-2. The observed quantity is the weight, \( W \), which can be expressed as

\[
W = g[m_s + m_a - m_c + m_t - m_{II} - \rho_f(V_{ads} + V_I - V_{II} - V_c)]
\]  
(1-10)

where \( g \) is the gravitation constant, \( m_s \) the mass of the adsorbent sample, \( m_a \) the mass adsorbed, \( m_c \) the mass of the counter weight, \( m_t \) the mass of the balance components (hang-down chain, sample pan, etc.) on the sample side, \( m_{II} \) the mass of the balance components on the reference side, \( V_{ads} \) the volume of the combined adsorbent/adsorptive system with mass \( (m_a + m_s) \), \( V_I \) and \( V_{II} \) the volumes of the balance components on the sample and reference sides, respectively, and \( V_c \) the volume of the counter weight. The volume terms in parentheses in eqn. (1-10) represent the total differential volume of the system. \( \rho_f \) is the density of the fluid adsorptive. Given the temperature and the pressure of the adsorptive, \( \rho_f \) can be calculated from the thermal equation of state.

\[
\rho_f = \rho_f(p, T)
\]  
(1-11)

In order to calculate the amount adsorbed, \( m_a \), from an experiment, a measurement is performed by removing both the adsorbent sample and the ballast from the microbalance, i.e. choosing \( m_s = m_a \). The new-observed weight can be presented

\[
W_0 = g[m_t - m_{II} - \rho_f(V_I - V_{II})]
\]  
(1-12)

By subtracting eqn. (1-12) from eqn. (1-10), the microbalance measurement delivers the excess weight

\[
\Omega = W - W_0 = g(m_s - \rho_f V_{ads})
\]  
(1-13)

Equation (1-13) consists of two unknown quantities, i.e. the mass adsorbed \( m_a \) and the "buoyancy volume" of the adsorptive/adsorbent system \( V_{ads} \). In principle, it is impossible to determine simultaneously both quantities from eqn. (1-13) without introducing a model or an assumption on either \( m_a \) or \( V_{ads} \), or providing other experiments leading to additional information on these quantities.

The basic assumption often made in the gravimetric technique is to identify \( V_{ads} \) with the so-called helium volume \( V_{He} \), which is independent of the pressure that the gaseous adsorptive is exerting on the adsorbent. \( V_{He} \) can be determined by helium adsorption measurements, and this leads to eqn. (1-14)

\[
\Omega_{He} = g(m_{He} - \rho_{He}V_{He})
\]  
(1-14)

where \( m_{He} \) is the mass of helium that adsorbs. The fluid densities for adsorptives can be calculated by using e.g. the Benedict-Webb-Rubin equation of state. By assuming that helium does not adsorb at all, then the helium volume, \( V_{He} \), can be simply obtained with eqn. (1-14).

It has been pointed out that this procedure, although commonly adopted, can lead to erroneous values for \( m_a \). One source of error is due to the assumption that \( V_{ads} = V_{He} \), because helium is small and can access micropores that larger adsorptive molecules cannot. A second source of error is due to the assumption that helium is not adsorbing. This assumption is fairly good at high temperatures, but is not strictly correct. A third and likely more significant
source of error is due to the fact that $\rho_{He}$ is quite small, even at relative higher pressures, which means that the uncertainty of the volume terms in eqn. (1-14) is quite large. These issues only become significant at high pressures, where fluid densities are high.

As a result of the above discussion, one should bear in mind that $V_{ads}$ normally depends on the adsorptive used and the pressure exerted by the adsorptive on the adsorbent system.

Another problem may be the determination of $\rho_r$. The density of an adsorptive fluid can be calculated easily and accurately using a specific equation of state if the experimental temperature and pressure conditions are far from the critical point. If this is not the case, $\rho_r$ should be determined simultaneously with the mass during the adsorption process. This problem is discussed in some published works on the measurement of high-pressure adsorption data. A concluding remark made is that an inadequate determination of $\rho_r$ can lead to dramatic errors, even if they are difficult to quantify. As for the in situ determination of $\rho_r$, several experimental methods are under development that should be very helpful in the determination of high-pressure adsorption data in the critical data.

Besides the above-mentioned problems, the errors of the gravimetric method can be also caused by the so-called Knudsen effect. The thermostat surrounds the balance pans from the sides and from the bottom. The thermomolecular flow has a maximum at a pressure, at which the mean free path of the gas molecules is comparable to a characteristic length, i.e. the diameter of the balance pan. In the usual arrangement of a microbalance with balance tubes with a diameter of 2 cm, the maximum thermomolecular flow is observed in the pressure range from 0.1 to 1 Pa. If the mean free path of the gas molecules is very much greater than the diameter of the balance tubes, the thermomolecular flow generates a pressure gradient, which can be described by eqn. (1-9). Therefore, the indicated pressure should be corrected, at least for operations at a lower pressure range.

Gravimetric methods can be used not only in equilibrium adsorption measurements but also in dynamic systems. The operation under flow conditions with the gravimetric microbalance has been carried out for several decades. However, it has been reported that strong temperature variations can be detected inside the adsorbent particle bed during the adsorption uptakes. In addition, data obtained by the gravimetric method are influenced by effects associated with flow patterns and bypassing, resulting in extensive corrections and inherently affecting the accuracy of the measurement.

1.4 Comparison of Volumetric and Gravimetric Methods

For the determination of the specific surface area with nitrogen at 77 K, Brunauer, Emmett, and Teller used a volumetric apparatus, and many investigators used a similar apparatus to measure the entire isotherm to determine the pore size distribution from the Kelvin equation. Soon afterwards, gravimetric techniques were applied to the determination of adsorption properties.

The volumetric method is used more widely because the apparatus is much simpler, can be cheaper, and is easier to use than the gravimetric microbalance technique. Gravimetric
measurements can hardly be performed without an electronic microbalance. The most complicated volumetric system is easier to operate and requires less painstaking technique than even the simplest of vacuum microbalances. On that account, therefore, the volumetric method is preferable to the gravimetric technique except in special circumstances.

On the other hand, the gravimetric method is more versatile. By simply replacing the liquid nitrogen bath by a furnace, one can perform measurements of controlled chemical reactions of the sample with a gas, as well as thermal decomposition or thermo-gravimetric analysis. Different investigations can be performed sequentially without having to remove the sample. Several examples of such measuring sequences have been reported in literature, e.g. degassing, adsorption properties (amount adsorbed, surface area, and pore size distribution, etc.), controlled reactions, followed by a second determination of adsorption properties, etc.

In addition, the gravimetric method has the outgassing advantages. The diameter of the tubes connecting the sample space to the vacuum pump can be much larger in the balance, compared to those in the volumetric technique. The sample bulb of a volumetric apparatus, usually, must be connected through a capillary tube in order to reduce the effect of variations in the level of the liquid nitrogen for measurements at low temperatures. This leads to a much more time-consuming outgassing procedure with higher residual gas pressure over the sample. Using the gravimetric method, the sample weight is continuously monitored, and therefore the rate and extent of the outgassing procedure can be controlled. The weight loss versus time curve may reveal temperature-dependent reactions of the material or decomposition. In addition, the outgassing procedure in the gravimetric technique enables the correction of the sample weight for the material lost during degassing. On the other hand, this correction would be very difficult indeed to estimate using the volumetric method.

The gravimetric method is well suited to measure adsorption isotherms in the region where the volumetric method is least accurate, namely, where the amount adsorbed is small compared to the amount unadsorbed; this condition may occur when the available surface area is small or the adsorptive forces are weak. Another, perhaps a special case, where the gravimetric method is advantageous is with the adsorption of liquid vapors such as water and ethanol ones, which are adsorbed strongly by glass surface, thus leading to inaccuracy in the volumetric determination of the adsorption isotherms. The gravimetric method minimizes this error.

In both methods, the most serious errors are related to calibrations. In the volumetric measuring method this error occurs in the calibration of the dead-space in the sample vessel, whereas in the gravimetric method it is the buoyancy error. Such errors for both techniques increase with operating pressure. However, the error cumulates in each step of the incrementally measured isotherm in the volumetric method.

Concerning dynamic measurements, both techniques have seriously similar drawbacks, i.e. the contact of gas or vapor with adsorbent material is unsatisfactory. Consequently, external mass transport limitations may be present in both techniques. In addition, it is hardly to maintain essentially isothermal conditions over the adsorbent bed due to heat effects. Over the past several decades the volumetric and gravimetric techniques have been dramatically improved and developed in the system sensitivity, operating range, and automation. However,
the above-mentioned drawbacks for the dynamic measurements have not been eliminated due to the limitations of their operating principles.

An attempt to accurately determine the mass uptake led to the continuous-flow method. This method is basically a modification of the chromatographic technique, in which the column packing is the adsorbent sample itself, and the mobile gas phase is a mixture of an inert gas and the adsorptive. Helium is generally used as the carrier gas. The sample removes the adsorptive from the gas stream, thus changing the composition of the mixture. This composition change is detected and recorded by a thermal sensor. The dynamic flow method has certain advantages over the volumetric and gravimetric techniques: the apparatus does not require high vacuum and the external mass transfer limitations over the sample bed and heat effects can be improved. It seems to be suitable for measuring the gas uptake. However, it has a major drawback that limits its use: the composition of the gas mixture must be accurately known. The determination of the accurate concentrations becomes complicated. Especially, for fast adsorption processes, measurements of the concentrations are almost impossible online.

1.5 Tapered Element Oscillating Microbalance

The first paper that described a new patented instrument, the tapered element oscillating microbalance (TEOM), was presented at the Division of Petroleum Chemistry, Inc., American Chemical Society, Houston Meeting, March 23-28, 1980. Patashnick and Rupprecht developed the TEOM technique for accurate, real-time monitoring of particulates in the effluents of combustion systems. The system continuously monitors a change in mass of an exchangeable filter cartridge as dust laden air or gas is drawn through it. The TEOM instruments are able for monitoring both high and low particulate concentrations for on-line operation. Low particulate concentrations are typically in the $\mu g m^{-3}$ range whereas high concentrations are typically in the $g m^{-3}$ range.

In the beginning of 90’s, Rupprecht & Patashnick Co., Inc. developed the TEOM series 1500 pulse mass analyzer, which was applied to laboratory investigations in heterogeneous catalysis. In the past decade, this novel technique has been rapidly used by both academic institutes and industrial research centers worldwide. The applications of this technique have been to catalyst deactivation, for instance, deactivation in the form of coking, and catalyst kinetics, e.g. diffusion, reaction, and adsorption kinetics.

In this section, the TEOM operating principles will be introduced in detail. Possible errors in determination of the mass change are analyzed. A brief review of literature is focused
on the applications of this novel technique. In addition, by combining our own experience, a comparison of the TEOM and the conventional gravimetric technique is made.

1.5.1 Principles
At the heart of the TEOM series 1500 PMA is a tapered element, which acts to provide a structure to constrain the sample in the test bed at its lower end, as well as to determine the mass change of the test material. A simplified schematic of the TEOM oscillating unit is shown in Figure 1-3. A measured carrier/reactant or adsorptive sample gas flow proceeds into the inlet line of the instrument, down through the tapered element, and then passes through the material test bed. A certain purge-gas flow, depending on the rate of the measured carrier/reactant or adsorptive sample-gas flow, passes down around the tapered element, preventing diffusion of the product gases or vapors back into the system and keeping the sample gas stream together as they exist from the tapered element. The outlet is commonly connected to a GC or mass spectrometer. Inside the sensor unit, two separate control zones maintain temperatures. The preheat zone governs the gas stream temperature in the upper part of the sensor unit. The main temperature control zone heats the tapered element and the sample bed where the reaction or adsorption takes place.

The active element of the TEOM consists of a tube constructed of proprietary glass material with a high mechanical quality factor and having a special taper. The tapered element oscillates in a clamped-free mode as a cantilever beam. Though the proper selection of the glass material, design, and drive system, this hollow tube can be set to vibrate at its natural (or resonant) frequency of oscillation. Figure 1-4 shows this feature.

It cannot be over-emphasized that the TEOM is significantly different from gravimetric and quartz crystal microbalances. The TEOM is an oscillator whose frequency can be described with two parameters; the restoring force constant (or the spring constant), $K$, and
the effective mass, \( m \), consisting of the mass of the sample, \( m_s \), the effective mass of the tapered tube, \( m_t \), and the sample loading, \( \Delta m \), in the tapered tube.

\[
m = m_s + m_t + \Delta m
\]  

The relation between these quantities is given by the expression:

\[
4\pi^2 f^2 = \frac{K}{m}
\]  

or

\[
f^2 = \frac{K_0}{m} \quad \text{with} \quad K_0 = \frac{K}{4\pi^2}
\]

The tapered element is kept in oscillation by a feedback system. The oscillator of the element is converted into an electrical signal by a light-emitting diode-phototransistor combination, the output of the phototransistor being modulated by the light-blocking effect of the vibrating element. Output of the phototransistor is amplified and fed back to the conductive coating on the tapered element. This AC signal interacts in the DC field produced by the field plates on either side of the tapered element and maintains the element at its natural (or resonant) frequency of oscillation.

If the mass \( \Delta m \) is determined gravimetrically and added to the sample holder, \( K_0 \) can be determined from the frequencies \( f_1 \) and \( f_2 \), where \( f_1 \) is the frequency without \( \Delta m \) and \( f_2 \) is the frequency with the sample loading mass \( \Delta m \). It is

\[
f_1^2 = \frac{K_0}{m_s + m_t} \quad \text{and} \quad f_2^2 = \frac{K_0}{m_s + m_t + \Delta m}
\]

From these two equations \( K_0 \) for a particular device can be calculated:

\[
K_0 = \Delta m \left( \frac{1}{f_1^2} - \frac{1}{f_2^2} \right)^{-1}
\]

When the mass of the material test bed increases, the natural oscillating frequency of the tapered element decreases, and \textit{vice versa}. By comparing the measured frequency to one stored at the beginning of the experiment, the system acquires an accurate and time resolved record of mass changes. If the TEOM is oscillating to start with at the frequency of \( f_s \) and exhibits the frequency \( f_0 \) after a mass uptake, \( \Delta m \) can be obtained as a function of \( f_0 \), \( f_s \), and \( K_0 \). It is

\[
\Delta m = K_0 \left( \frac{1}{f_0^2} - \frac{1}{f_s^2} \right)
\]

Note that equation (1-20) is independent of the sample mass, \( m_s \), and the effective mass, \( m_t \), of the tapered oscillating element.
1.5.2 Apparatus and experimental procedures

A Rupprecht & Patashnick TEOM 1500 mass analyzer (100-mg sample volume) was set-up for measurements of adsorption, diffusion, and reaction in house. The experimental set-up is schematically illustrated in Figure 1-5. The usual pattern followed in experiments is to regenerate a given solid sample and then carry out adsorption, reaction, and/or desorption with continuous monitoring of the mass changes. The oscillating microbalance is connected through a data acquisition board to a personal computer, with data acquisition software LabView.

![Flow diagram of the experimental set-up.](image)

The supply rates of the liquid are controlled in the range from 0.03 to 0.6 g h⁻¹ by a so-called μ-Flow mass-flow meter (Bronkhorst, High-Tech B.V.). At room temperature, the liquid can be drawn from a pressurized container with an inert gas blanket and measured by the liquid mass-flow meter. The required flow rate is controlled to the set-point value by a control valve (C) forming an integral part of the liquid flow and carrier gas mixing valve (M). Then the formed mixture is subsequently led into the evaporator to achieve total evaporation (E). This explains the abbreviation of “CEM”, shown in Figure 1-5, viz.: Controller-Evaporation-Mixing, the three basic functions of the liquid delivery system. The main features of this liquid delivery system are a) accurately controlled gas/liquid mixture, b) fast response, c) high reproducibility, d) very stable vapor flow, and e) flexible selection of gas/liquid ratio.

Helium is the most suitable carrier gas. Sometimes other gases, like argon, nitrogen, etc., can be used under the certain conditions, at which their adsorption is likely to be negligible.
The gas manifold uses Brooks mass-flow controllers to deliver metered amounts of carrier and feed gases. After mass-flow controllers, all streams can be heated by heat tracings if necessary. This is essential to prevent condensation for gases with lower vapor pressures at room temperature. The partial pressure of a feed gas is determined by its fraction of the total molar-feed-flow rate through the sample bed and the total pressure. A mixture of carrier gas and adsorptive gas is used to establish partial pressures below ambient pressure and pure gas is used for pressures above ambient pressure. The outlet of the sample bed is directed to a backpressure regulator for maintenance of the system pressure. Part of the sample bed effluent is split either to vent or the inlet of the analysis unit such as a GC or mass spectrometer.

The sample bed is usually loaded with a thin layer of a powder material, which weight can vary from 10 to 80 mg. Quartz wool that is considered as an inert material for most gases or vapors is used at the top and the bottom of the sample bed to keep the adsorbent particles firmly packed, which is essential for a stable measurement.

Prior to experiments the powder material can be outgassed by in situ heating in flowing carrier gas in order to remove adsorbed impurities. The absence of contamination during this procedure is indicated by the absence of a sample mass change. Thereafter, the sample is allowed to cool under carrier gas to the temperature desired for the experiments. For equilibrium adsorption experiments, isotherm data are obtained by a stepwise increase of the partial pressure of adsorptive at fixed temperatures. The feed is maintained until the sample is equilibrated as indicated by constant mass change. Desorption can be performed to check whether adsorption is reversible.

Based on the operating principle of the TEOM, the total mass uptake consists of the amount adsorbed and the mass change caused by the change of the gas density in the tapered tube.

\[
\Delta m = \Delta m_a + \Delta m_g
\]  

(1-21)

where \(\Delta m_a\) is the adsorbed mass and \(\Delta m_g\) is the change in the gas density determined by measuring a mass change during a reference run under the same conditions. From eqn. (1-21)

![Figure 1-6 Measurements of the isotherm data of propene on DD3R at 303 K. (a) Mass changes on DD3R (48.7 mg); (b) reference run in the sample bed filled with 55 mg of quartz wool; (c) data obtained by subtracting the reference run (b) from the total mass change (a).](image-url)
it follows that a mass change is measured with respect to the conditions at the beginning of the experiment. At the start of every experiment the mass is set to zero. The frequency is in the order of 53 Hz.

The change in the gas density depends on the type of gas and the operating conditions. To correct for the mass change caused by the change in the density of the gas phase reference experiments have to be performed. In a reference experiment the response of the TEOM is measured without adsorption taking place. Two different reference experiments were performed with 55 mg quartz wool and no sample. No significant difference in the mass change was observed among these two reference runs. In addition, the relationship between the mass change in the reference runs and the partial pressure of the adsorbing gas is almost linear. No exact correlation, however, was found for different gases to be able to rely on a kind of master curve for this correction.

The spring constant $K_0$ is a weak function of the temperature. The change in the spring constant with temperature over the range of 303 to 525 K corresponds with a maximum mass change of 10 µg. For the series of isotherms this means that an error of less than 1% is introduced by going from the lowest temperature (303 K) to the highest temperature (525 K).

Figure 1-6 shows an example for measurements of the isotherm data of propene on DD3R at 303 K. It is clearly seen that the contribution of the change in the gas density to the total mass change is negligible at lower pressures, whereas this contribution becomes significant at higher pressures.

In transient operations, a high flow rate of carrier gas through the sample bed is always required to minimize mass and heat transfer limitations in the sample bed. Due to a high flow through the sample bed, changing the total flow rate will cause a change in the system pressure. Therefore, nearly constant flows are always maintained in transient experiments. This essentially minimizes the experimental errors caused by the system pressure change. Figure 1-7 illustrates the apparent mass change caused by the change in the total flow rate.

![Figure 1-7 Transient responses in the reference runs of propane with a flow rate of 24.14 cm³ (NTP) min⁻¹ (NTP: room temperature and 101.3 kPa) at 303 K in flowing He with a rate of 200 cm³ (NTP) min⁻¹ through the sample bed filled with 55 mg of quartz wool. (a) Propane flow switch-on; (b) propane flow switch-off; (●) pressure change; (▲) mass change.](image)
Figure 1-8 Comparison of the raw total mass (RTM) and averaged total mass (ATM). (a) No difference in a longer span time; (b) significant difference in the initial stage.

through the sample bed (see also chapter 5).

Once a frequency point is computed in the control unit and is passed to LabView, it is stored in an internal program array that holds the recent data points. When the user selects an averaging time, all the frequency points taken over the averaging time period are averaged together. This value is used as the average frequency. For a typical ten-second averaged time, this can include 12 values at an approximate 0.84 s gate time. After an initial averaging period is used to determine a "zero mass" or reference frequency $f_0$ in eqn. (1-20), the new raw or average frequencies are used to determine new raw total mass (RTM) or average total mass (ATM) values. In data files, both the RTM and ATM values are available for viewing and plotting. The RTM has the proper time resolution and is the result of individual frequency readings taken at gate time intervals. Therefore, for fast uptakes or desorption processes, the RTM reflects the transient behavior. For equilibrium measurements the ATM can be used. Figure 1-8 shows the difference between RTM and ATM in the initial stage.

1.5.3 Possible errors
The TEOM performance is quantified in terms of the normalized standard deviation (NSD) and in terms of a baseline drift. The normalized standard deviation is a relative number and is used to confirm that the sample is secure in the packed bed and that no mechanical or electrical noise is interfering with the operation of the balance. The NSD is used to compute the system's 'random noise' and depends on the recording duration (averaging time). At a typical ten-second averaging time with 12 recording values (at an approximate 0.84 s gate time), the NSD value is as low as $3 \times 10^{-6}$. The expected NSD value is higher for shorter gate times. During the equilibrium and transient adsorption and/or desorption measurements a gate time of 0.84 s is commonly used. Therefore, the accuracy of measurement of the mass uptake with the TEOM is determined by the baseline drift. Under operating conditions a stable baseline can be achieved and the absolute baseline drift is usually within the range of 10 µg over one week.

Although the TEOM microbalance measurements are accurate to 1 µg, certain total mass changes are required in order to reduce the uncertainty in experiments. Figure 1-9 gives an example to illustrate this concern. For 2,3-dimethylbutane on silicalite-1 at 473 K and 1.94 kPa, some random noises appear in the adsorption curve, as shown in Figure 1-9a. Even
Figure 1-9 Uptakes (RTM data) of adsorptive vapors in flowing He with a rate of 100 cm$^3$ (NTP) min$^{-1}$ in silicalite-1 crystals (20.4 mg). (a) 1.94 kPa of 2,3-dimethylbutane at 473 K; (b) 0.458 kPa of n-hexane at 373 K.

Though the equilibrium adsorption data can be read without a considerable error, some uncertainties will be introduced to the determination of diffusivity from the uptake curve. In contrast, for a strong adsorptive, even at higher temperatures and lower partial pressures, very stable equilibrium adsorption data and smooth uptake curves can always be obtained with the TEOM. The adsorption of n-hexane on silicalite-1 at 373 K shows this example, illustrated in Figure 1-9b. Therefore, a minimum mass change of 0.1 mg is required to have a good accuracy in the TEOM, although smaller values can be determined.

In addition, the experimental uncertainty will be introduced if the total mass change is comparable to that caused by the change in the gas density, especially for adsorption of weaker adsorptives operated at higher pressures.
1.5.4 Comparison with the gravimetric method
The TEOM technique, in principle, has similar advantages as the gravimetric method. The microbalance measurements are accurate to 1 µg. Because the TEOM technique is based on inertial instead of gravimetric forces to measure the amount adsorbed, this technique has several advantages for measurements of transient behaviors in microporous materials over the gravimetric method:

(1) A well-defined gas phase due to a high gas-flow rate of feed with carrier gas through the adsorbent bed. This improves the external mass and heat transfer for microporous materials and also results in a fast response to gas phase changes.\(^{22}\)

(2) A high mass resolution across the entire range: a low system standard deviation and a stable baseline. These properties are hardly influenced by a change in experimental conditions, resulting in accurate and reproducible measurements.

(3) Experimental conditions can be varied over a wide range of pressure and temperature, relevant to practical operations.

It is noted that Kapteijn \textit{et al.}\(^{23}\) explored also a packed-bed balance reactor suspended from an electronic microbalance via flexible tubing. This eliminated the mass- and heat transfer issues, but the sensitivity amounted to 1 mg and there was a considerable baseline drift. Especially the latter precluded further developments. A comparison of the TEOM with the conventional microbalance is summarized in Table 1-1.

<table>
<thead>
<tr>
<th>TEOM</th>
<th>Conventional Microbalance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow-through packed sample bed.</td>
<td>Flow around and over sample pile.</td>
</tr>
<tr>
<td>Flow rates up to 2000 cm(^3) min(^{-1}) without degrading resolution.(^a)</td>
<td>Flow rates greater than 100 cm(^3) min(^{-1}) can cause noise.</td>
</tr>
<tr>
<td>No reduction in mass resolution at high temperatures and high pressures.</td>
<td>Significant reduction in mass resolution at high temperatures.</td>
</tr>
<tr>
<td>Response time of 0.1 s.</td>
<td>Response time of 10 to 30 s.</td>
</tr>
<tr>
<td>Standard operation 300-873 K and 0-1 MPa.(^b)</td>
<td>Standard operation 300-1300 K and 0-0.1 MPa.</td>
</tr>
<tr>
<td>Separation of electronics and reactor.</td>
<td>Reactor and electronics in the same chamber.</td>
</tr>
<tr>
<td>No buoyancy phenomena.</td>
<td>Static electricity may affect the sample cup.</td>
</tr>
<tr>
<td>Temperature programming not well-established.</td>
<td>Buoyancy phenomena.</td>
</tr>
<tr>
<td>Temperature programming application.</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Flow rates used lower than 300 cm\(^3\) (NTP) min\(^{-1}\) in this study. \(^b\) Extended to 973 K and 6 MPa.
1.5.5 Applications

Since Rupprecht and Patashnick invented the TEOM 1500 series analyzer, some work associated with this technique has been reported worldwide. For instance, simultaneous measurements of adsorption, reaction, and coke information were investigated by Hershkowitz and Madiera\textsuperscript{24}, Chen et al.\textsuperscript{25-28}, and Liu et al.\textsuperscript{29} Rekoske and Barteau\textsuperscript{30} and Petkovic and Larsen\textsuperscript{31} used this technique to investigate catalytic kinetics. Equilibrium adsorption properties of microporous materials have been carried out by Zhu et al.\textsuperscript{32-35} Rebo et al.\textsuperscript{36} used the TEOM technique to measure the diffusivities of toluene, \textit{o}-xylene, and \textit{p}-xylene in HZSM-5 zeolite.

Catalyst deactivation in the form of coking is a major topic in current catalyst research. Coking can be rapid and compensated by continuous regeneration, as in FCC catalysts, or slow and the subject of monthly or yearly maintenance, as in hydrotreating catalysts. The TEOM has both the short term mass resolution and long term stability to study these phenomena. Coking kinetics and the associated study of purging rates, conversion rates, regeneration rates, required temperatures, selectivity, and yield can all benefit by knowing the mass changes of the catalyst bed very precisely in real time. Figure 1-10 shows an example for coke formation as a function of time during the hydrodechlorination of 1,2-dichloropropane over an activated carbon supported Pt-Cu catalyst.\textsuperscript{37} In the initial step a rapid mass increase in the catalyst bed is attributed to the adsorption of 1,2-dichloropropane. A steady increase of coke deposited on the catalyst can be observed during the entire reaction period investigated; after about 90 hours, ca. 15 wt.% of coke was formed, as shown in Figure 1-10.

The formed coke can modify the catalyst texture, mainly due to blocking micropores, resulting in a low adsorption capacity. With the TEOM, adsorption properties can be determined. Figure 1-11 illustrates the effects of the formed coke and of the \textit{in situ} reduction on the adsorption capacity for 1,2-dichloropropane. The adsorption capacity in the coke deposited catalyst can significantly decrease. The TEOM can also serve as temperature-programmed reduction (TPD) to reduce the catalyst \textit{in situ} before the reaction. The reduced catalyst can lead to the higher amount adsorbed for 1,2-dichloropropane. This might be

![Figure 1-10 Coke formation on Pt-Cu/C during the hydrodechlorination of 1,2-dichloropropane (1,2-DCP) at 543 K and 3.4 kPa for either 1,2-DCP or H\textsubscript{2} in flowing N\textsubscript{2}.](image-url)
Figure 1-11 Comparison of the isotherm data of 1,2-dichloropropane on the fresh and spent Pt-Cu/C catalysts at 303 K. The dashed line represents the difference in the amount adsorbed on catalysts after and before reduction. (A) Remaining amount adsorbed after desorption in flowing N₂ on the reduced sample.

attributed to chemisorption of 1,2-dichloropropane on the metallic species. It is also worthy to mention that the adsorption reversibility can be easily checked by desorption in flowing carrier gas with the TEOM. The adsorption of 1,2-dichloropropane on the reduced catalyst was irreversible; a constant mass change of 0.5 mol kg⁻¹ was measured after desorption in 24 hours. This value is in remarkable agreement with the difference in the amount adsorbed for the adsorption of 1,2-dichloropropane on the material after and before reduction. This also confirms the presence of chemisorption on the reduced catalyst.

The above example indicates that the TEOM is a versatile technique for application in the catalysis field. As a relatively new technique, its applications are still being explored and developed. The TEOM technique applied to measurements of adsorption and diffusion properties of microporous materials will be discussed and evaluated throughout this thesis.

1.6 Conclusions

A detailed description of the TEOM technique, including its operating principles and experimental procedures, has been given. Well-defined gas-solid phase conditions can be established in the TEOM due to a high flow rate of adsorptive and/or reactant gas in carrier gas through the sample bed. This, in principle, can significantly improve external mass and heat transfer limitations for microporous materials. In addition, experimental conditions in the TEOM can approach those of practical relevance to temperature, pressure, and flow. Therefore, the TEOM technique can circumvent most of the problems associated with either the volumetric or the gravimetric methods and is suited for typical engineering application research like adsorption and uptake determinations with microporous materials and catalyst deactivation studies.
References

Equilibrium Adsorption of Light Alkanes in Silicalite-1

The equilibrium adsorption of the light alkanes methane, ethane, propane, \textit{n}-butane, and isobutane in silicalite-1 has been investigated using the TEOM technique. Either a conventional or a dual-site Langmuir isotherm appropriately describes the equilibrium data. Good agreement with the literature data determined by other techniques indicates that the TEOM is a reliable technique. The adsorption of isobutane in silicalite-1 reveals the discrete preferential molecular siting, implying a discrete-dual-structural heterogeneity for light alkanes in silicalite-1.

This chapter is based on the following publication:
2.1 Introduction

Adsorption data of components are of utmost importance for a good design of separation units based on differences in thermodynamics or in kinetic properties. Often data are obtained by either a volumetric method or a gravimetric method. Both methods have their advantages and disadvantages, and generally large corrections have to be made on the raw experimental data.

Recently, a new method has been commercialized, in which the mass change of a vibrating tube is determined by frequency measurements, the so-called tapered element oscillating microbalance (TEOM) mass analyzer. The main feature of the TEOM technique is an oscillating element that is based on inertial instead of gravimetric forces to measure the amount adsorbed. An important advantage of this technique is that the gas which has to adsorb flows through a packed bed of adsorbent material. So, external mass transport limitations are nearly absent in this technique. In addition, it is easy to maintain essentially isothermal conditions. Therefore, the TEOM can be used not only for steady state measurements, but also for transient uptake and desorption experiments.

![Diagram of silicalite-1 structure](image)

Figure 2-1 Schematic of silicalite-1 structure. After Krishna and Paschek.1

Of the many existing zeolitic structures, silicalite-1 is perhaps the most studied, best characterized and the most widely used in practice.1 Silicalite-1 has a high ratio of silica to alumina, is hydrophobic and stable up to high temperatures. It provides a non-polar structure for adsorption of relatively small molecules. Figure 2-1 shows a schematic of the structure of silicalite-1 which consists of a system of intersecting channels composed of zigzag channels along x, cross-linked by straight channels along y. Both channels are defined by 10-rings. The straight channels are approximately elliptical in shape having a 0.53 nm × 0.56 nm cross section while the zigzag channels have a 0.51 nm × 0.55 nm cross section, see Figure 2-1.

This chapter discusses the measurements of single component adsorption isotherms in silicalite-1 crystals using the TEOM technique. An interpretation of the difference between the isotherm of isobutane and the isotherms of the normal alkanes is given. The conventional and the dual-site Langmuir isotherm models have been used to describe the adsorption data.
In addition, thermodynamic properties, like the isosteric heat and entropy of adsorption calculated from the isotherms, are presented to characterize interactions between adsorptive and adsorbent.

2.2 Experimental

A Rupprecht & Patashnick TEOM 1500 pulse mass analyzer (100 mg sample volume) was used in an experimental set-up designed for measurement of equilibrium adsorption in microporous materials such as zeolites. The active element of the TEOM consists of a tube constructed of a material having a special taper. A feed back system maintains the oscillation of the tapered tube. The natural frequency will change in relation to the mass in the tapered tube. The mass uptake is then determined by the change of the oscillating frequency. Software and hardware provided by R&P perform the required frequency counting and mass calculation. A LabView program is used to operate the set-up and to record the results. A detailed description of the TEOM apparatus is available in chapter 1 of this thesis.

The tapered element was loaded with 47 mg of silicalite-1 crystals. Quartz wool was used at the top and the bottom of the sample bed to keep the adsorbent particles firmly packed, which is essential for a stable measurement.

With the TEOM both pressure and temperature programmed runs can be performed. The isotherms were obtained by a step-wise increase of the partial pressure of the feed gas at fixed temperatures. The isobaric experiments were performed by temperature programmed runs at a fixed pressure. The partial pressure of the feed gas was determined by its fraction of the total molar-feed-flow rate through the sample bed and the total pressure. A mixture of helium and the adsorptive gas was used to create partial pressures below 101.3 kPa, and pure gas was used for pressures above 101.3 kPa.

When the partial pressure of the gas phase was changed, it took about 1 to 5 minutes to reach steady state. If the mass did not change for more than 1% in 2 minutes, equilibrium was assumed. This procedure was repeated and about every 10 minutes a new partial pressure could be set for most conditions. The amount adsorbed was then calculated by subtracting the reference run from the results obtained with the silicalite-1 crystals in the sample holder.

The silicalite-1 crystals with a ratio Si/Al > 1300 were supplied by Prof. dr. J.C. Jansen

Figure 2-2 Scanning electron micrographs of the silicalite-1 sample used in this study.
(TU Delft). The template inside the silicalite-1 crystals was removed by calcination at 873 K for 12 hours. The apparent density of the sample was 1.76 g cm\(^{-3}\) and the adsorption of N\(_2\) indicated an accessible microporous void volume of 0.179 cm g\(^{-1}\) and a microporous area of 372 m\(^2\) g\(^{-1}\). The crystal size was about 120 \(\times\) 50 \(\times\) 50 \(\mu\)m \((L \times H \times W)\), as determined by SEM, shown in Figure 2-2.

Prior to the experiments the crystals were outgassed in the following way. After a temperature rise with a rate of 10 K min\(^{-1}\) \textit{in situ} in a helium flow rate of 200 cm\(^3\) (NTP) min\(^{-1}\) (NTP: room temperature and 101.3 kPa), the sample was heated at 498 K for 2 hours in order to remove adsorbed impurities.

Helium was obtained as an ultra-high purity gas (>99.999%). The gaseous adsorptives such as methane, ethane, propane, \(n\)-butane, and isobutane were 3.5 grade (>99.95%).

The isotherm data were measured in the temperature range 303 to 408 K. Four temperatures were used for each adsorptive to reduce the uncertainty in the derived thermodynamic properties. Most experiments were duplicated, and both adsorption and desorption experiments were performed to confirm reversibility.

### 2.3 Results and Discussion

#### 2.3.1 Isotherms

The isotherms of the first four \(n\)-alkanes and isobutane adsorbed in silicalite-1 are shown in Figures 2-3 to 2-7. The isotherms were reversible over the complete pressure range investigated. For the sake of clarity, the desorption points are omitted. The isotherms of the four \(n\)-alkanes exhibit a type-I adsorption isotherm (Brunauer classification) over the temperature and pressure range studied. For the adsorption isotherm of isobutane at low temperatures a deviation from the type-I behavior is seen in Figure 2-7. A two-step adsorption behavior is observed for the isotherm obtained at 303 and 338 K. This has recently also been reported by Sun \textit{et al.}\(^2\). In Figure 2-8 results are given for the isobars of \(n\)-butane and isobutane at 50 kPa over the temperature range of 303 to 525 K. A clear difference in the

![Figure 2-3 Adsorption isotherms of methane in silicalite-1. Lines are the Langmuir isotherm model fits. (Φ) 303 K; (▲) 338 K; (●) 373 K; (▽) 408 K.](image)
Figure 2-4 Adsorption isotherms of ethane in silicalite-1. Lines are the Langmuir isotherm model fits. (✦) 303 K; (▲) 338 K; (●) 373 K; (▼) 408 K.

Figure 2-5 Adsorption isotherms of propane in silicalite-1. Lines are the Langmuir isotherm model fits. (✦) 303 K; (▲) 338 K; (●) 373 K; (▼) 408 K.

temperature dependence of the two isomers is observed.

A comparison of our isotherm data with the literature data determined by different methods is compiled into Table 2-1. The measurement conditions of pressure and temperature and the measurement techniques are also given. Considering the differences in pressure and temperature, loadings of all the adsorbatives investigated agree quite well with each other. Figure 2-9 also shows a comparison of our data and the data from Sun et al.\textsuperscript{2} for the butane isomers in the complete pressure range at 303 K. As is apparent in Figure 2-9, our results are in good agreement with the data from Sun et al.\textsuperscript{2}, determined by the gravimetric method.

The adsorption equilibrium data of ethane and propane by Hampson and Rees\textsuperscript{3} with the isosteric method and of methane by Golden and Sircar\textsuperscript{4} with the volumetric method are also given in Table 2-1. Under similar conditions, our results are also in good agreement with these literature data. Abdul-Rehman et al.\textsuperscript{5} measured the equilibrium adsorption of C\textsubscript{1}-C\textsubscript{4} normal alkane in Linde S-115 silicalite with the volumetric technique. For methane and ethane, good agreement is seen in Table 2-1. However, for propane and n-butane, our results
Figure 2-6 Adsorption isotherms of $n$-butane in silicalite-1. Lines are the Langmuir isotherm (solid) and the DSL model (dashed) fits. (●) 303 K; (▲) 338 K; (●) 373 K; (▼) 408 K.

Figure 2-7 Adsorption isotherms of isobutane in silicalite-1. Lines are the Langmuir isotherm (solid) and the DSL model (dashed) fits. (●) 303 K; (▲) 338 K; (●) 373 K; (▼) 408 K.

are much higher than the data from Abdul-Rehman et al.\textsuperscript{5} As pointed out by Sun et al.\textsuperscript{2}, these differences may be related to the samples; pure crystals of uniform shape and size were used in this study while Abdul-Rehman et al.\textsuperscript{5} used silicalite-1 pellets with a binder. In addition, we found that the adsorption capacity of silicalite-1 is also related to the sample preparation. The remaining template in the sample can significantly decrease the adsorption capacity. Compared to our previous results of the same systems in silicalite-1 calcined at 723 K,\textsuperscript{6} the capacities of the present silicalite-1 for the adsorptives investigated are higher by about 20%. We attribute that to a difference in remaining template fragments.
### Table 2-1 Isotherm data: comparison of different experimental techniques

<table>
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<tr>
<th>Method</th>
<th>$T$ (K)</th>
<th>$p$ (100 kPa)</th>
<th>$q$ / mol kg$^{-1}$</th>
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<td></td>
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<td></td>
</tr>
<tr>
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<td>1.952</td>
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$n$-butane

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<th>$q$ / mol kg$^{-1}$</th>
</tr>
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isobutane

<table>
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<th>$q$ / mol kg$^{-1}$</th>
</tr>
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<td>1.420</td>
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</table>

$^a$ TEOM data at the same pressure as that in the literature and at 303 K.

Figure 2-8 Isobars of $n$-butane and isobutane in silicalite-1 at a pressure of 50 kPa. Also given are isotherm results. Closed symbols: data from isobars; open symbols: data from isotherms.
Figure 2-9 Comparison of \(n\)-butane and isobutane isotherm data with data from literature. Closed symbols: this study at 303 K; open symbols: data at 308 K from Sun et al.\(^2\)

Figure 2-10 Saturation amounts adsorbed, fitted with the Langmuir model, for the normal alkanes as a function of temperature. (○) Methane; (△) ethane; (●) propane; (▼) \(n\)-butane.

In general, there is a tendency for adsorptive molecules to locate in the smaller channels to maximize their attractive interactions with the silicalite-1. If the diameters of the adsorbed molecules are too large, this will lead to repulsion constraints and the molecules will reside in the larger intersections.\(^7\)

For the regular three-dimensional silicalite-1 micropore structure it is instructive to express the preferential location in terms of molecules per unit cell. In silicalite-1 crystals each unit cell consists of four segments of straight channels, four segments of zigzag channels, and four segments of channel intersections.\(^8\) The size of an isobutane molecule, with a kinetic diameter of 0.5 nm, is comparable to the diameters of both the straight and the zigzag channels. In this case the repulsion between isobutane molecules and the channel wall dominates over the attractive interaction between the adsorptive and the adsorbent. Therefore, isobutane molecules prefer to reside in the larger intersections.

Molecular simulations show that single-branched alkanes prefer to reside in the channel intersections and that the linear alkanes indeed reside in the channels.\(^7, 9\) The difference
Figure 2-11 Isobutane adsorption capacity in the intersections, fitted with the DSL model for the isotherms at 303 and 338 K and the Langmuir model for the isotherms at 373 and 408 K, as a function of temperature. The dashed line represents a theoretical value of 0.693 mol kg⁻¹.

between the channels and the intersections is much larger than the difference between the two types of channels. This means that one can say that essentially two different adsorption locations exist in silicalite-1.

To describe this difference of adsorptive location a dual-site Langmuir model has been proposed.⁶,¹⁰-¹³ This model takes into account the geometrical constraints of the zeolite pore structure and the different interaction potential in the channels and the intersections of the silicalite-I crystals

\[
q = q_{\text{sat},C} \frac{K_C p}{1 + K_C p} + q_{\text{sat},I} \frac{K_I p}{1 + K_I p}
\]  

(2-1)

with the subscripts C and I refer to the channels and intersections, respectively. The geometrical constraints give rise to two different saturation amounts adsorbed in locations C and I and indicated by \( q_{\text{sat},C} \) and \( q_{\text{sat},I} \). In the case of low loadings, adsorptive molecules reside in the energetically preferred locations. In that case, the dual-site Langmuir model simplifies to the well-known Langmuir model.

\[
q = q_{\text{sat}} \frac{K p}{1 + K p}
\]  

(2-2)

The isotherms of methane, ethane, propane in silicalite-1 are well described by the conventional Langmuir model, as shown in Figures 2-3 to 2-5. For the isotherms of n-butane in silicalite-1 only small deviations from the Langmuir model are found at 303 and 338 K (Figure 2-6). With increasing loading, n-butane molecules gradually occupy the intersections, resulting in the deviation from the Langmuir model. Consequently, at the low temperatures the isotherms of n-butane are better described by the dual-site Langmuir model. The estimated saturation amounts of the normal alkanes in silicalite-1 for the Langmuir model are presented in Figure 2-10. In the low temperature range, the fitted \( q_{\text{sat}} \) values stay reasonably constant for all the normal alkanes. However, at high temperatures \( q_{\text{sat}} \) is a function of temperature and slightly decreases with an increase in the operating temperature. This behavior emphasizes a difficulty in applying site concepts in a strict way. But the Langmuir model is generally used
to describe adsorption isotherms. Barrer pointed out that the Langmuir model is often satisfactory for zeolites, due to compensation effects, even for more heterogeneous systems.

It is interesting to note that the isotherm for isobutane (Figure 2-7) exhibits a two-step adsorption behavior at 303 and 338 K. A preferential packing of 4 isobutane molecules per unit cell corresponds to a loading of 0.693 mol kg\(^{-1}\) for the intersections. From the model fitting we have an estimated adsorption capacity for the intersections, \(q_{int}\), is in good agreement with this value (Figure 2-11). This explains the change in the adsorption behavior of isobutane. For a loading above the saturation amount in the intersections the adsorbing molecules are forced at higher pressures into the straight or zigzag channels. If the dual-site Langmuir model is fitted to the results obtained at a high temperature one of the two terms becomes negligibly small.

Isobaric adsorption data of \(n\)-butane and isobutane in silicalite-1 are shown in Figure 2-8. The \(n\)-butane isobar shows the typical trend obtained with the Langmuir isotherm model. The isobar for isobutane at 50 kPa exhibits a two-step behavior. Over the temperature range of 303 to about 400 K, the isobar for isobutane is clearly different from the result obtained for \(n\)-butane. For the isobaric adsorption of isobutane, the decrease in the amount adsorbed is initially steeper with increasing temperature. This indicates that, if the temperature is increased, first the isobutane molecules residing in the channels desorb and that at higher temperatures the isobutane molecules are removed from the intersections. These results confirm the existence of the change of the adsorptive location with a change in the loading of isobutane in silicalite-1. Apparently, the large difference between the adsorption interaction for isobutane in the channels and in the intersections results in a clear two-step adsorption behavior. This molecular location of isobutane in the micropores of silicalite-1 crystals was further confirmed by simulations,\(^9,13,15\) as shown in Figure 2-12. A comparison with the isothermal results at the same pressure, obtained from different experimental runs, shows good agreement.

The various results, presented in Figures 2-3 to 2-8, show that the temperature and the branching have a pronounced effect on the adsorption of light alkanes in silicalite-1. For the

![Figure 2-12 Probability of isobutane at 0.1 kPa (left) and at 100 kPa (right) in silicalite-1 at 300 K. The zigzag channels are from the left to the right, and the straight channels are perpendicular to the zigzag channels. These figures were obtained by plotting the centers of mass of the molecules (dots) every 500 Monte Carlo cycles.\(^15\)]
adsorption of \(n\)-butane and isobutane, the smallest alkane isomers, in silicalite-1 a molecular shape effect is observed.

2.3.2 Thermodynamic properties
The isotherms have been used for the estimation of thermodynamic adsorption parameters. The isosteric heat of adsorption \(Q^{	ext{st}}\) is defined by eqn. (2-3).

\[
\left[ \frac{\partial \ln p}{\partial T} \right]_q = \frac{Q^{	ext{st}}}{RT^2}
\]  

(2-3)

\(Q^{	ext{st}}\) can be obtained from a plot of \(\ln p\) vs \(1/T\). Extrapolation then gives the isosteric heat of adsorption for the limiting case of adsorption at zero coverage. The calculated isosteric heat of adsorption at zero coverage is independent of the temperature. A comparison of the derived quantity \(Q^{	ext{st}}\), the isosteric heat of adsorption at zero coverage, is regarded as a useful way to check the temperature dependence of the initial slopes of the isotherms. The results in Table 2-2 show that the present data of the isosteric heat of adsorption agree well with chromatographic data and calorimetric results.

Figure 2-13 shows the results of the isosteric heat of adsorption as a function of the amount adsorbed for the adsorbives investigated. For the normal alkanes, the values of \(Q^{	ext{st}}\) almost stay constant in the complete range of the amount adsorbed. This indicates that silicalite-1 is energetically homogeneous for the adsorption of the normal alkanes. Figure 2-13 also gives the result of the isosteric heat of adsorption for isobutane at loadings up to 0.693 mol kg\(^{-1}\), corresponding to adsorption in the intersections.

If \(Q^{	ext{st}}\) and the adsorption enthalpy are assumed to be identical by neglecting any small temperature dependence, the differential molar entropy, \(S_{\text{ads}}\), of adsorbives in the adsorbed phase can be calculated by eqn. (2-3).

![Figure 2-13 Isosteric heat of adsorption as a function of the amount adsorbed for all the adsorbives investigated in silicalite-1. (✦) Methane; (▲) ethane; (●) propane; (▼) \(n\)-butane; (●) isobutane.](image-url)
Figure 2-14 Differential entropy in the adsorbed phase as a function of the amount adsorbed for all the adsorbents investigated in silicalite-1 at 303 K. Points correspond to the data calculated from eqn. (2-4). (●) Methane; (▲) ethane; (⚫) propane; (▽) n-butane; (◆) isobutane.

\[
\bar{S}_{ads} = S^0_s(298.15) + \int_{298.15}^{T} C_p \frac{dT}{T} + R \ln \left( \frac{P_0}{p} \right) - \frac{Q^0}{T}
\]  

(2-4)

where \(S^0_s(298.15)\) is the standard molar entropy of the gas phase at \(T = 298.15\) K and \(p_0 = 101.3\) kPa. \(C_p\) is the molar heat capacity of gaseous adsorbents at constant pressure and \(T\) and \(p\) are the pressure and temperature under the equilibrium conditions. \(S^0_s\) and \(C_p\) are obtained from literature. Values of \(\bar{S}_{ads}\) were determined at each of the experimental temperatures for all the adsorbents and were plotted as a function of the amount adsorbed. The results at 303 K are illustrated in Figure 2-14. The values of \(\bar{S}_{ads}\) increase with temperature and decrease with increasing loading. The curves of \(\bar{S}_{ads}\) at different temperatures of the individual components never intersect and follow parallel courses. For isobutane, the strongest decrease in the differential molar entropy in the adsorbed phase is seen as loadings up to the adsorption capacity in the intersections (0.693 mol kg\(^{-1}\)).

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>(Q^0_s / \text{kJ mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>this study</td>
</tr>
<tr>
<td>methane</td>
<td>17.7</td>
</tr>
<tr>
<td>ethane</td>
<td>32.4</td>
</tr>
<tr>
<td>propane</td>
<td>43.6</td>
</tr>
<tr>
<td>n-butane</td>
<td>50.3</td>
</tr>
<tr>
<td>isobutane</td>
<td>47.3</td>
</tr>
</tbody>
</table>

\(^a\) Gas chromatographic method.\(^b\) Calorimetric method.
It is clear that entropy effects play a role in the preferential siting in the intersections for isobutane. With an increase in the amount adsorbed above 0.693 mol kg$^{-1}$, the adsorbing molecules are forced into the channels. Therefore, more degrees of freedom are lost, resulting in an additional loss of the entropy. This is further elaborated in chapter 3.

2.4 Conclusions

With the inertial microbalance technique, TEOM, it is possible to accurately measure equilibrium adsorption in microporous materials such as zeolites over a wide pressure and temperature range relevant to practical applications. The adsorption isotherms of methane, ethane, propane, $n$-butane, and isobutane in silicalite-1 have been obtained using this technique. Agreement with the literature data determined by other techniques indicates that the TEOM is a reliable technique. The isosteric heats of adsorption for all the adsorptives at zero coverage derived from the isotherm data are in good agreement with those determined by calorimetric and chromatographic methods.

The molecular geometry affects the adsorptive location within the micropores. By comparing the amount adsorbed with a preferential packing for isobutane, deviations from the Langmuir model have been explained. The isotherms of isobutane deviating from the Langmuir model can be well fitted by a dual-site Langmuir model, based on two adsorption locations. Adsorption of isobutane in silicalite-1 exhibits a two-step behavior according to both isothermal and isobaric results. The adsorption of isobutane in silicalite-1 reveals the discrete-dual-structural heterogeneity for light alkanes in silicalite-1. Due to geometrical constraints isobutane first fills the intersections followed by filling of the channels. Molecular simulations support this picture.

Acknowledgements

I am indebted to Prof. dr. J. C. Jansen for supplying the silicalite-1 sample, to Dr. L. J. P. van den Broeke and Dr. J. M. van de Graaf for fruitful discussions, and to Dr. ir. T. J. H. Vlugt for CBMC simulations.

References

Interaction Potential Topology of Alkane Molecules within Silicalite-1 Micropores: A Dual-Site Langmuir Approach

The reconciliation of the experimental data, the adsorption isotherms of light alkanes in silicalite-1 at multiple temperatures, and molecular simulations provides an excellent interpretation of the adsorption in terms of a volume filling process with two different spaces. This can be described by a dual-site Langmuir expression. The derived thermodynamic properties like adsorption enthalpy and entropy are in good agreement with those determined by other techniques in literature. The observed two-step adsorption behavior for isobutane in silicalite-1 is attributed to the large difference in the adsorption entropy between the molecular locations in the intersections and in the channels.

This chapter is based on the following publication:
3.1 Introduction

Silicalite-1 is a well-characterized microporous zeolite structure having a high ratio of silica to alumina. It is hydrophobic and stable up to high temperatures. Silicalite-1 provides a nonpolar structure for adsorption of relatively smaller gas molecules.\(^1\) It is, therefore, considered as a model adsorbent for testing adsorption isotherm models, based on gas-solid molecular interactions.\(^2\) A number of investigators have measured the equilibrium adsorption data of light alkanes in silicalite-1.\(^2-11\) Others have been interested in studying the behavior of adsorbed molecules inside silicalite-1 at a molecular level with molecular simulations.\(^12-23\)

Extensive studies in adsorption in silicalite-1 have shown that the molecular shape and size of an adsorptive can significantly affect molecular locations in the channels and intersections of silicalite-1, resulting in different adsorption behaviors. Various isotherm models have been proposed to describe isotherm data. In general, four kinds of models have been used in adsorption in silicalite-1. The Langmuir model has been often used to fit the adsorption data of light alkanes in silicalite-1.\(^7,8,11\) Barrer\(^24\) pointed out that the Langmuir model is usually satisfactory for zeolites, due to compensation effects, even for more heterogeneous systems. However, most fitting results show that the estimated adsorption capacity is a function of temperature and often decreases with increasing temperature,\(^8,11\) whereas the void fraction in the zeolite does hardly change.

The second type of isotherm models is based on the virial equation.\(^3,10\) Most adsorption isotherms are indeed well described by the virial equation. However, this model is relatively complicated and often there is a lack of physical interpretation of some parameters in the model. In addition, it has been found that the adsorption isotherms of branched alkanes largely deviate from the virial domain.\(^10\)

The so-called dual-site Langmuir model has also been used to describe the isotherms that deviate from the conventional Langmuir model.\(^11\) This model is especially suitable for fitting the isotherm data of branched alkanes in silicalite-1. Recently, Krishna \textit{et al.}\(^14\) and Vlugt \textit{et al.}\(^18\) have used this model to describe the simulation data. The fitting results seem to be "perfect". However, a similar problem has arisen: the total fitted saturation amount adsorbed is a function of temperature.

Chiang and co-workers\(^25-28\) have investigated the adsorption of benzene and \(p\)-xylene in ZSM-5 zeolites and pointed out that with two types of channels and the intersections there are three kinds of adsorption "sites". Per unit cell four occurrences of each of these three sites are considered. This number is called the "magic" number by Olson and Reischman,\(^29\) because it represents the number of intersections, the number of straight channels, and the number of the zigzag channels per unit cell in silicalite-1. Adsorption equilibria on these three sites are described by the quasi-chemical equilibria:

\[ A + S_j \leftrightarrow AS_j \quad j = 1,\ldots,n \]  

(3-1)

where \(A\) is an adsorptive molecule in the gaseous phase, \(S_j\) is a vacant site \(j\) in the solid, \(n\) is the number of sites, and \(AS_j\) is an adsorbed molecule on site \(j\) in the solid. Then, by assuming no interactions, the isotherm is obtained from the following equation:
\[ q = 4 \sum_{j=1}^{n} \frac{K_j p}{1 + K_j p} \]  

(3-2)

where \( q \) is the amount adsorbed in molecules per unit cell, \( K_j \) the adsorption equilibrium constant for equilibrium \( j \), and \( p \) the partial pressure of the adsorbate in the gaseous phase. The adsorption isotherms of \( C_4-C_7 \) straight and branched alkanes are well fitted with this isotherm model.\(^5\)-\(^6\) However, we have found that the "magic" number as the saturation number of molecules per unit cell of silicalite-1 is only valid for adsorbive molecules within the certain range of molecular size. From volume filling considerations, it is easily realized that the adsorption capacity in silicalite-1 is a function of molecular size.

Recently, molecular simulations have been used to investigate adsorption in zeolites in order to interpret interactions between adsorptive and adsorbent.\(^12\)-\(^23\) Experimentally, the determined adsorption capacity of silicalite-1 is significantly affected by various factors such as sample preparation methods and measurement techniques.\(^10\) In molecular simulations, a "perfect" silicalite-1 sample is used. Therefore, the data of the simulated adsorption capacity can be considered as "ideal" values. This chapter presents a reconciliation of these molecular simulations and high quality data, measured with a novel technique-TEOM, for the adsorption of light alkanes in silicalite-1. This approach is further validated by derived thermodynamic properties, adsorption enthalpies and entropies, for a dual-site Langmuir model (DSL).

3.2 Theoretic Considerations

3.2.1 Adsorption capacity and molecular packing in silicalite-1.
Various experimental studies have been done in the adsorption of light alkanes in silicalite-1. However, most experiments have been performed at relatively low pressures. The derived adsorption capacity, therefore, varies with the isotherm models used. Recently, Sun \textit{et al.}\(^10\) have reported the isotherm data of methane and ethane at 277 K and pressures up to 2 MPa. These results seem to be very useful to ascertain the adsorption capacities for these molecules.

![Figure 3-1 Comparison of measured amounts adsorbed at 277 K from Sun \textit{et al.}\(^10\) (closed symbols) and adsorption capacity determined by CBMC simulations from Vlugt \textit{et al.}\(^18\) (open symbols) for light alkanes in silicalite-1.](image)
Figure 3-2 Comparison of isobutane isotherm data to data from the literature. (●) This study at 303 K; (Δ) experimental data from Sun et al.\textsuperscript{10} at 308 K; (O) CBMC-simulation data from Vlugt et al.\textsuperscript{17} at 300 K.

in silicalite-1. Figure 3-1 shows the maximum loadings measured at 277 K for methane, ethane, propane, n-butane, and isobutane from Sun et al.\textsuperscript{10} For ethane, propane, n-butane, and isobutane, the reported maximum loading reaches the adsorption capacity. In Figure 3-1 are included the results of the adsorption capacity simulated by the configurational-bias Monte Carlo (CBMC) technique.\textsuperscript{18} As is apparent in Figure 3-1 the experimental results are in fair agreement with the data from the simulations for linear C\textsubscript{2}-C\textsubscript{4} alkanes and isobutane. For methane in silicalite-1, there is no experimental adsorption capacity available in literature.

Table 3-1 Maximum loadings measured for adsorption in silicalite-1 at 303 K

<table>
<thead>
<tr>
<th>Adsorptive</th>
<th>$p \times 10^5$ Pa</th>
<th>$q_{max}$ mol kg$^{-1}$</th>
<th>m.u.c.$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane</td>
<td>5.065</td>
<td>1.506</td>
<td>8.69</td>
</tr>
<tr>
<td>ethane</td>
<td>4.052</td>
<td>2.287</td>
<td>13.2</td>
</tr>
<tr>
<td>propane</td>
<td>4.052</td>
<td>2.023</td>
<td>11.7</td>
</tr>
<tr>
<td>n-butane</td>
<td>1.925</td>
<td>1.677</td>
<td>9.81</td>
</tr>
<tr>
<td>isobutane</td>
<td>1.925</td>
<td>1.552</td>
<td>8.96</td>
</tr>
</tbody>
</table>

$^a$ Molecules per unit cell.

Table 3-1 shows the experimental data of the maximum loading, determined by the TEO, for the investigated light alkanes in silicalite-1 at 303 K, presented in chapter 2 of this thesis. For propane and the butane isomers, the measured maximum loading almost reaches the adsorption capacity. These results are in good agreement with the data from Sun et al.\textsuperscript{10} and the simulation results from Vlugt et al.\textsuperscript{18} As an example, Figure 3-2 shows this comparison for isobutane in silicalite-1.

The diameters of the channels and intersections of silicalite-1 do not allow two molecules to occupy positions adjacent to each other spanning the channel or intersection diameter, even for molecules as small as N\textsubscript{2}.\textsuperscript{31} Therefore, a single molecule is expected to adsorb on the
channel or intersection wall so as to provide the maximum interaction with the surface.

Based on the above experimental data and simulation results, the adsorption capacities for light alkanes in silicalite-1 are drawn out. Following Richards and Rees\textsuperscript{8}, the saturation amount can be split up into the number of molecules located in the channels and in the intersections as indicated in Table 3-2. The proposed molecular locations are based on the length of the channels and of the intersections as well as on the adsorptive molecular size. Molecular simulations confirmed these numbers and indicate that single- branched alkanes prefer to reside in the channel intersections and that the normal alkanes indeed prefer to reside in the channels.\textsuperscript{12, 17-18, 32} These preferential locations are taken into account to describe the adsorption in silicalite-1.

Table 3-2 Theoretical number of molecular packing in the straight (S) and zigzag (Z) channels and intersections (I) per unit cell of silicalite-1

<table>
<thead>
<tr>
<th>Adsorptive</th>
<th>Molecules</th>
<th>Total</th>
<th>S</th>
<th>Z</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane</td>
<td></td>
<td>18</td>
<td>6</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>ethane</td>
<td></td>
<td>16</td>
<td>4</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>propane</td>
<td></td>
<td>12</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>n-butane</td>
<td></td>
<td>10</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>isobutane</td>
<td></td>
<td>10</td>
<td>2</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

3.2.2 Isotherm model

Drago and co-workers\textsuperscript{31, 33-38} proposed that adsorption processes in microporous materials could be determined by a series of distribution type equilibria involving pores with different widths relative to the molecular diameter of the adsorptive. This model accounts for the heterogeneity of microporous materials. For a series of equilibria, expressed in eqn. (3-1), the adsorption isotherm is given by eqn. (3-3)

\[
q = \sum_j \frac{q_j^{\text{sat}} K_j p}{1 + K_j p}
\]  

(3-3)

where \(K_j\) is an equilibrium constant describing adsorption process \(j\), \(q_j^{\text{sat}}\) is the capacity for process \(j\), and \(p\) is the pressure of the adsorptive in the gaseous phase. The authors pointed out that eqn. (3-3) is similar in form to the Langmuir equation but is conceptually very different. The equilibrium constants for physical adsorption are in fact distribution coefficients involving the gaseous adsorptive in equilibrium with adsorbed molecules within the pores of the solid. Therefore, each \(K_j\) may be considered as an average value that covers a narrow range of pore sizes.

In silicalite-1 there are two types of channels and the intersections available for adsorption. The difference between the channels on the one hand and the intersections on the other hand is much larger than the difference between the two types of channels. As a first approximation essentially two different adsorption locations exist in silicalite-1. Following Drago and co-workers\textsuperscript{31, 33-38}, Chiang and co-workers\textsuperscript{25-28}, and Millot \textit{et al.}\textsuperscript{5-6}, we apply the dual-site
Langmuir (DSL) isotherm model to describe the adsorption of light alkanes in silicalite-1.

\[ q = q_{c}^{\text{sat}} \frac{K_{c} p^*}{1 + K_{c} p^*} + q_{i}^{\text{sat}} \frac{K_{i} p^*}{1 + K_{i} p^*} \]  

(3-4)

In eqn. (3-4), \( q \) is the amount adsorbed in molecules per unit cell, \( q_{c}^{\text{sat}} \) the capacity for adsorption in the channels, and \( q_{i}^{\text{sat}} \) the capacity for adsorption in the intersections. The capacity for adsorption in either the channels or the intersections depends on the adsorptive molecular size and the value for the investigated alkanes is given in Table 3-2. \( K_{c} \) and \( K_{i} \) are the equilibrium constants for adsorption in the channels and in the intersections, respectively. The dimensionless pressure, \( p^* \), is expressed by eqn. (3-5),

\[ p^* = \frac{p}{p_0} \]  

(3-5)

where \( p \) is the partial pressure of the adsorptive in the gaseous phase and \( p_0 \) is the standard reference pressure of \( 1.013 \times 10^5 \) Pa.

In this way the adsorption equilibrium constants \( K_j \) are dimensionless and their temperature dependency can be expressed as:

\[ K_j = \exp \left( \frac{\Delta S_{j}^{\text{ads}}}{R} - 1 \right) \cdot \exp \left( \frac{-\Delta H_{j}^{\text{ads}}}{RT} \right) \]  

(3-6)

### 3.3 Results and Discussion

#### 3.3.1 Adsorption isotherms

Experimental adsorption data for silicalite-1 are given in Figures 3-3 to 3-7, and the DSL isotherms are given by the solid lines. The estimated values of the adsorption equilibrium constants for each temperature, \( K_{c} \) and \( K_{i} \), are listed in Table 3-3 for all systems studied. These values were obtained by nonlinear regression of the experimental data on the DSL

![Figure 3-3 Isotherms of methane in silicalite-1. Lines are the isotherm model fits by a simple Langmuir expression. (三角形) 303 K; (△) 338 K; (○) 373 K; (▽) 408 K.](image)

Figure 3-3 Isotherms of methane in silicalite-1. Lines are the isotherm model fits by a simple Langmuir expression. (三角形) 303 K; (△) 338 K; (○) 373 K; (▽) 408 K.

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Figure 3-4 Isotherms of ethane in silicalite-1. Lines are the isotherm model fits by eqn. (3-4). (●) 303 K; (▲) 338 K; (○) 373 K; (▼) 408 K.

Figure 3-5 Isotherms of propane in silicalite-1. Lines are the isotherm model fits by eqn. (3-4). (●) 303 K; (▲) 338 K; (○) 373 K; (▼) 408 K.

model, eqn. (3-4), using the fixed values of the saturation loadings, given in Table 3-2. For methane, the experimentally adsorbed amounts were too far from the saturation loading to allow a distinction between channels and intersections. Therefore, a simple Langmuir expression was used with the channel adsorption capacity, since adsorption in the intersections does not apply at these conditions. For the other gases the saturation loading was better approached. For n-butane the observed capacity was only 2% below the theoretical value, indicating the quality of the silicalite-1 used. This allowed a statistically significant distinction between the adsorption locations in the channels and in the intersections, leading to quite different values of the equilibrium constants.

The isotherms of the first four normal alkanes adsorbed in silicalite-1 exhibit a type-I adsorption isotherm, according to the Brunauer classification, over the temperature and pressure range studied. For the adsorption isotherm of isobutane at low temperatures, a deviation from the type-I behavior is seen in Figure 3-7. A “kink” is observed for the isotherm obtained at 303 and 338 K. The same observation has been recently reported by Sun et al.\textsuperscript{10}
Figure 3-6 Isotherms of n-butane in silicalite-1. Lines are the isotherm model fits by eqn. (3-4). (●) 303 K; (▲) 338 K; (○) 373 K; (▼) 408 K.

Figure 3-7 Isotherms of isobutane in silicalite-1. Lines are the isotherm model fits by eqn. (3-4). (●) 303 K; (▲) 338 K; (○) 373 K; (▼) 408 K.

for the isobutane/silicalite-1 system. The molecular simulations have also shown a two-step adsorption behavior for branched alkanes in silicalite-1.\textsuperscript{14,17-18} The simulated results indicate that there is a clear difference between normal alkanes and branched alkanes in the probability distribution of adsorptive molecules residing in the channels and the intersections.\textsuperscript{17-18} The difference is striking. The branched alkanes have a strong preference for the intersections, whereas, linear alkane molecules have a more or less preferential distribution to reside in the channels.

There are four intersections per unit cell in silicalite-1. At loadings below four molecules per unit cell, the isotherms of isobutane indeed show a type-I adsorption behavior and isobutane occupies only the intersections, corresponding to the isotherms at high temperatures in Figure 3-7. However, above a loading of four molecules per unit cell, a second adsorption step develops and isobutane molecules are filling the channels. This is more demanding and requires a significantly higher driving force (pressure), resulting in a two-step adsorption
behavior.\textsuperscript{17}

Table 3-3 Estimated values and standard deviation of adsorption equilibrium constants [eqn. (3-4)]

<table>
<thead>
<tr>
<th>$T$</th>
<th>$q_{C}^{\text{sat}}$</th>
<th>$K_C$</th>
<th>$q_{1}^{\text{sat}}$</th>
<th>$K_1$</th>
<th>$\sigma_{\text{model}}$\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>m.u.c.\textsuperscript{b}</td>
<td></td>
<td>m.u.c.\textsuperscript{b}</td>
<td></td>
<td>m.u.c.\textsuperscript{b}</td>
</tr>
<tr>
<td>methane\textsuperscript{c}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>14</td>
<td>0.303 ± 0.002\textsuperscript{d}</td>
<td></td>
<td></td>
<td>0.144</td>
</tr>
<tr>
<td>338</td>
<td>14</td>
<td>0.145 ± 0.001</td>
<td></td>
<td></td>
<td>0.063</td>
</tr>
<tr>
<td>373</td>
<td>14</td>
<td>0.079 ± 0.000</td>
<td></td>
<td></td>
<td>0.027</td>
</tr>
<tr>
<td>408</td>
<td>14</td>
<td>0.048 ± 0.000</td>
<td></td>
<td></td>
<td>0.013</td>
</tr>
<tr>
<td>ethane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>12</td>
<td>8.00 ± 0.15</td>
<td>4</td>
<td></td>
<td>0.217 ± 0.015\textsuperscript{d}</td>
</tr>
<tr>
<td>338</td>
<td>12</td>
<td>1.95 ± 0.03</td>
<td>4</td>
<td></td>
<td>0.085 ± 0.007</td>
</tr>
<tr>
<td>373</td>
<td>12</td>
<td>0.618 ± 0.016</td>
<td>4</td>
<td></td>
<td>0.040 ± 0.010</td>
</tr>
<tr>
<td>408</td>
<td>12</td>
<td>0.239 ± 0.005</td>
<td>4</td>
<td></td>
<td>0.020 ± 0.007</td>
</tr>
<tr>
<td>propane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>8</td>
<td>134 ± 14</td>
<td>4</td>
<td></td>
<td>13.8 ± 2.4</td>
</tr>
<tr>
<td>338</td>
<td>8</td>
<td>20.2 ± 0.8</td>
<td>4</td>
<td></td>
<td>2.90 ± 0.13</td>
</tr>
<tr>
<td>373</td>
<td>8</td>
<td>4.36 ± 0.12</td>
<td>4</td>
<td></td>
<td>0.819 ± 0.037</td>
</tr>
<tr>
<td>408</td>
<td>8</td>
<td>1.22 ± 0.02</td>
<td>4</td>
<td></td>
<td>0.287 ± 0.014</td>
</tr>
<tr>
<td>n-butane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>8</td>
<td>2169 ± 270</td>
<td>2</td>
<td></td>
<td>31.9 ± 8.4</td>
</tr>
<tr>
<td>338</td>
<td>8</td>
<td>216 ± 2</td>
<td>2</td>
<td></td>
<td>4.16 ± 0.06</td>
</tr>
<tr>
<td>373</td>
<td>8</td>
<td>33.2 ± 0.9</td>
<td>2</td>
<td></td>
<td>0.796 ± 0.08</td>
</tr>
<tr>
<td>408</td>
<td>8</td>
<td>7.03 ± 0.04</td>
<td>2</td>
<td></td>
<td>0.202 ± 0.006</td>
</tr>
<tr>
<td>isobutane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>6</td>
<td>2.15 ± 0.08</td>
<td>4</td>
<td></td>
<td>1411 ± 390</td>
</tr>
<tr>
<td>338</td>
<td>6</td>
<td>0.145 ± 0.002</td>
<td>4</td>
<td></td>
<td>213 ± 5</td>
</tr>
<tr>
<td>373</td>
<td>6</td>
<td>0.016 ± 0.004</td>
<td>4</td>
<td></td>
<td>45.9 ± 2.3</td>
</tr>
<tr>
<td>408</td>
<td>6</td>
<td>0.003 ± 0.000</td>
<td>4</td>
<td></td>
<td>12.8 ± 0.4</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Standard deviation model: $\sqrt{\sum_n (q_{cal} - q_{exp})^2 / (n - j)}$, for $j$ fitting parameters. \textsuperscript{b} Molecules per unit cell. \textsuperscript{c} Fitted by a simple Langmuir expression. \textsuperscript{d} 95% confidence error.
3.3.2 Thermodynamic properties

The equilibrium constants, $K_C$ and $K_I$, quantify the adsorption interaction of a given adsorptive with an adsorbent. The magnitudes of the equilibrium constants depend on both the properties of the adsorptive and of the adsorbent, and correspond to the affinity of the adsorptive to the adsorbent. From the fitted $K_C$ and $K_I$, the adsorption enthalpies and entropies can be obtained via the Van't Hoff equation, eqn. (3-6). The ln $K_C$ and ln $K_I$ as a function of $1/T$ are shown graphically in Figures 3-8 and 3-9. The linearity of these plots indicates that meaningful thermodynamic parameters result from the DSL isotherm model. The adsorption enthalpy and entropy are obtained from a combined regression of all experimental data for ethane, propane, $n$-butane, and isobutane on eqns. (3-4) and (3-6). The results are given in Tables 3-4 and 3-5. The obtained thermodynamic parameters satisfy thermodynamic principles, a loss of enthalpy and entropy upon adsorption, and have magnitudes expected for physisorption.\textsuperscript{39}

An extensive comparison of the experimental heats of adsorption for normal alkanes has

![Figure 3-8](image)

**Figure 3-8** ln $K_C$ as a function of $1/T$ for the adsorption of light alkanes in the channels of silicalite-1. (●) Methane, equilibrium constant fitted by a simple Langmuir expression; (▲) ethane; (●) propane; (▼) $n$-butane; (◇) isobutane.

![Figure 3-9](image)

**Figure 3-9** ln $K_I$ as a function of $1/T$ for the adsorption of light alkanes in the intersections of silicalite-1. (▲) Ethane; (●) propane; (▼) $n$-butane; (◇) isobutane.
been given by Vlugt et al.\textsuperscript{18}. The range of the reported heat of adsorption is also shown in Table 3-4. Most of the experimental data for methane in silicalite-1 are in the range from 18 to 22 kJ mol\textsuperscript{-1}. For ethane the experimental data center around a value of 31 kJ mol\textsuperscript{-1} and for propane around a value of 41 kJ mol\textsuperscript{-1}. For \textit{n}-butane, most experimental data are around 51 kJ mol\textsuperscript{-1}. The literature data of the adsorption heat are mostly related to adsorption techniques at low loadings and for the linear alkanes they should therefore be compared with the enthalpy of adsorption in the channels. Considering the lower enthalpies for the intersections, this might explain the range in literature data (Table 3-4).

Only Millot \textit{et al.}\textsuperscript{5-6} have reported the adsorption enthalpy and entropy for isobutane, determined by a temperature-programmed-equilibration method (TPE), i.e. a temperature-programmed desorption (TPD) technique, in which equilibrium conditions are maintained. At a starting loading of six molecules per unit cell for isobutane in silicalite-1 at 303 K, the TPE curve shows two peaks: the peak at a lower temperature corresponds to the desorption of the molecules residing in the channels and the second peak at a higher temperature represents the desorption of the molecules located in the intersections. Therefore, two series of the adsorption enthalpy and entropy have been obtained. These results are included in Table 3-5. Our results of the derived adsorption entropy are in fair agreement with the data from Millot \textit{et al.}\textsuperscript{5} The values of the derived adsorption enthalpies and entropies for the two locations exhibit significant differences. The size of an isobutane molecule, with a kinetic diameter of 0.5 nm,\textsuperscript{40} is comparable with the diameter of either the straight or zigzag channels. On the other hand, there is more space to accommodate isobutane molecules in the intersections. It has been noticed that the three-methyl groups of an isobutane molecule penetrate particularly in two side channels and a straight channel, optimizing the Van der Waals interaction.\textsuperscript{41} This might explain the similar magnitude of the adsorption enthalpies of propane in the channels and isobutane in the intersections. This partial occupation of the channel space by the isobutane in the intersection bears implications for the adsorption of \textit{n}-butane and isobutane mixtures.\textsuperscript{42} The initial filling of the channels by \textit{n}-butane and the intersections by isobutane will consequently not be independent processes due to the spatial phenomena, and non-ideal behavior is expected. Unfortunately, experimental data are not yet available to confirm this. Recently, Krishna and Paschek\textsuperscript{42} used CBMC simulations to predict the isotherm of a 50:50 mixture of \textit{n}-butane and isobutane in silicalite-1 at 300 K. A curious maximum in the loading of isobutane is shown in the mixture isotherm. In order to understand the mixture behavior they separately simulated the loadings of the mixture in the straight channels with the intersections and in the zigzag channels at 100 kPa. The results show that the isobutane molecules survive the mixture battle only at the intersection sites. These branched molecules are located nowhere else.
Table 3-4 Estimated adsorption enthalpy and entropy values for linear light alkanes in silicalite-1 for the combined fittings of the adsorption data. Also are given the literature data of the isosteric heat of adsorption

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>(-\Delta H^\text{ads}_C)</th>
<th>(-\Delta H^\text{ads}_1)</th>
<th>(Q^\text{st} a)</th>
<th>(-\Delta S^\text{ads}_C)</th>
<th>(-\Delta S^\text{ads}_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane</td>
<td>18.0 ± 0.1(^b)</td>
<td>18.1-28</td>
<td>61.1 ± 0.5(^b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ethane</td>
<td>34.4 ± 0.4</td>
<td>22.8 ± 3.1(^b)</td>
<td>29.9-45</td>
<td>87.8 ± 1.1</td>
<td>79.5 ± 10.0(^b)</td>
</tr>
<tr>
<td>propane</td>
<td>45.9 ± 0.7</td>
<td>37.9 ± 1.3</td>
<td>36.5-46.5</td>
<td>103 ± 2</td>
<td>94.9 ± 3.9</td>
</tr>
<tr>
<td>(n)-butane</td>
<td>56.1 ± 0.8</td>
<td>49.5 ± 2.0</td>
<td>48-54.8</td>
<td>113 ± 2</td>
<td>126 ± 6</td>
</tr>
</tbody>
</table>

\(^a\) Range of the experimental heats of adsorption summarized by Vlugs et al.\(^{18}\) 95% confidence error.

Table 3-5 Estimated adsorption enthalpy and entropy values for isobutane in silicalite-1 for the combined fittings of the adsorption data. Also are given the literature data of the adsorption enthalpy and entropy

<table>
<thead>
<tr>
<th>(-\Delta H^\text{ads}_C)</th>
<th>(-\Delta H^\text{ads}_1)</th>
<th>(-\Delta S^\text{ads}_C)</th>
<th>(-\Delta S^\text{ads}_1)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>kJ mol(^{-1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65.6±1.6</td>
<td>46.0 ± 1.3</td>
<td>202 ± 5</td>
<td>83.2 ± 3.5</td>
<td></td>
</tr>
<tr>
<td>44.9</td>
<td>50.2</td>
<td>143.6</td>
<td>88.2</td>
<td></td>
</tr>
</tbody>
</table>

Compared to the adsorption in the intersections, more degrees of freedom are lost, as isobutane molecules are completely located in the channels, resulting in an additional loss of the entropy (Table 3-5). This entropy effect might play a role in the change of the adsorption enthalpy as isobutane molecules are forced into the channels. Low-energy bending of the O-Si-O angles can lead to some flexibility in the channel dimensions of silicalite-1,\(^{31}\) which leads to a confined packing of isobutane molecules. Consequently, the interactions between isobutane and channel wall are enhanced, resulting in the larger adsorption enthalpy, compared to that in the intersections.

Although less pronounced regarding the difference in the adsorption entropy between the molecular locations in the channels and in the intersections, a similar effect is observed for \(n\)-butane for the filling of the intersectional space. Even though four intersections per unit cell exist, only two \(n\)-butane molecules are involved in the last space filling process. The length of the \(n\)-butane molecule is larger than that of the straight channels, so the molecules will partially extend into the intersectional space, leaving only room for one additional molecule. Three molecules in line will then occupy two intersections and two straight channel parts. This squeezing in of the last two \(n\)-butane molecules leads to a well-ordered packing with less degrees of freedom and more entropy loss (Table 3-4).

Recently, Drago et al.\(^{34}\) attempted to predict completely the adsorption of methane and ethane in HZSM-5. The adsorption capacities used were based on either the adsorptive dependent surface areas or the adsorptive dependent pore volumes of the adsorbent, while the adsorption constants were derived either from the Van der Waals' constant, \(a\), or from an assumed constant ratio of \(\Delta H^\text{ads}/\Delta S^\text{ads}\) for the adsorbent. Globally, a reasonable prediction is
obtained, but accurate descriptions are not possible since it leaves out of consideration on the different adsorption locations and associated thermodynamic properties.

The approach followed here to describe the adsorption of light alkanes in silicalite-1 is in fact based on a volume filling process, distinguishing globally two different spaces, the channels and the intersections. Depending on the geometry and size of the adsorbing molecule, either the channels or the intersections are filled first. Due to geometrical constraints the filling of the residual space in case of the larger butane molecules will affect the position of the already adsorbed molecules, which have to squeeze in a little, resulting in a more ordered structure. Therefore a major difference is expected in the entropy. For ethane and propane this is not the case. The more space in the intersections, the less loss of the adsorption entropy. In addition, the lower interaction with the wall in the intersections leads to a major difference in the adsorption enthalpy for the linear molecules.

The volume filling approach, combined with the theoretical values for the number of molecules that take up the space eliminates the need to estimate the latter from experimental data. Due to extrapolation a decreasing capacity is always observed with increasing temperature. Since this is generally much larger than that can be accounted for by a thermal expansion of the adsorbed phase, this was physically not sound. Fixing these values results in a better determination of the adsorption parameters and derived thermodynamic properties, and even allows distinction between channels and intersections. This demonstrates the power of combining experimental work with molecular simulations in interpreting adsorption in zeolites.

3.4 Conclusions

The reconciliation of the experimental data, the adsorption isotherms for light alkanes in silicalite-1 accurately measured with the novel TEOM technique at multiple temperatures, and molecular simulations provides an excellent interpretation of the adsorption in terms of a volume filling process with two different spaces. This can be described by a dual-site Langmuir expression.

The derived thermodynamic properties like the enthalpies and entropies associated with adsorption in the channels and in the intersections are physically sound and, in good agreement with the literature data as far as available. The observed two-step adsorption behavior for isobutane in silicalite-1 is attributed to the large difference in the adsorption entropy between the molecular locations in the intersections and in the channels. The credibility of the proposed approach is enhanced by its ability to provide meaningful thermodynamic properties.
References

41 T. J. H. Vlugt, personal communication.
Equilibrium Adsorption of Linear and Branched C₆ Alkanes in Silicalite-1

The equilibrium adsorption of linear and branched C₆ alkanes n-hexane, 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane in silicalite-1 has been investigated using a novel technique-TEOM. For n-hexane, a small "kink" in the isotherm is observed at about four molecules per unit cell of silicalite-1. The measured isotherms of both 2-methylpentane and 3-methylpentane at 303 K for the first time show the second step adsorption at loadings over four molecules per unit cell. A two-step adsorption behavior is confirmed for single branched C₆ alkanes. This observation is in good agreement with the picture of two distinct adsorption locations for single branched alkanes in silicalite-1 indicated by other techniques. The maximum loading for 2,3-dimethylbutane is about four molecules per unit cell under the conditions investigated and the molecules completely reside in the intersections. A dual-site Langmuir expression appropriately describes the equilibrium data for n-hexane, 2-methylpentane, and 3-methylpentane, while the isotherms of 2,3-dimethylbutane can be described by the Langmuir model. The derived thermodynamic properties such as adsorption enthalpy and entropy agree with those available determined by other techniques. The observed two-step adsorption behavior for single branched C₆ alkanes in silicalite-1 is attributed to the large difference in the adsorption entropy between the molecular locations in the channel intersections and in the zigzag channels.

This chapter is based on the following publication:
4.1 Introduction

One of the main applications of zeolitic materials is in the separation of mixtures based on different mechanisms, such as steric, equilibrium, and kinetic ones.\textsuperscript{1} In the equilibrium mechanism zeolites have micropores with different abilities to accommodate different molecules. In general, the stronger adsorbing species are preferentially removed by the adsorbent.

Silicalite-1 is the aluminum-free form of the ZSM-5 zeolite. Therefore it is hydrophobic.\textsuperscript{2} This characteristic can be used to selectively adsorb nonpolar hydrocarbon molecules in water for environmental applications.\textsuperscript{3} It is also considered as a good model adsorbent for testing adsorption isotherm models, based on gas-solid molecular interactions.\textsuperscript{4}

Branched hydrocarbons are preferred to straight-chain ones as ingredients in gasoline because branched hydrocarbons have a higher octane number. Catalytic isomerization has been used to convert straight-chain hydrocarbons to their mono- or di-branched structures. However, the product of catalytic isomerization is a mixture of linear and branched hydrocarbons that are in thermodynamic equilibrium, and the separation of linear hydrocarbons from their branched isomers becomes necessary. Recently, the separations of linear and branched C\textsubscript{6} mixtures through silicalite membranes have been carried out by Noble and co-workers\textsuperscript{5-7} and Matsufuji \textit{et al.}\textsuperscript{8} A very high selectivity for normal hexane over branched isomers has been reported. Furthermore, at elevated temperatures the flux of branched isomers exhibited a curious maximum with increasing partial pressure. Krishna and Paschek\textsuperscript{9} used the configurational-bias Monte Carlo (CBMC) simulations to calculate the pure component and mixture isotherms at various temperatures. By applying the Maxwell-Stefan theory for zeolite diffusion, they provided a nearly quantitative explanation of the separation data through the silicalite-1 membranes. The high selectivity for the separation of n-hexane from branched ones is primarily caused by the exclusion of the branched molecules. The reason for this exclusion was found in configurational entropic effects, i.e. for the branched isomers in silicalite-1 there is a large difference in the adsorption entropy between the molecular locations in the intersections and in the channels. Indeed, an extensive study by CBMC simulations shows a two-step adsorption behavior for branched alkanes in silicalite-1.\textsuperscript{10-14}

Two distinct adsorption sites for branched alkanes, one within the channel interiors and one at the intersections of the straight and zigzag channels, have been confirmed using FT-Raman sectroscopy\textsuperscript{15} and temperature-programmed desorption\textsuperscript{16-18}. Sun \textit{et al.}\textsuperscript{19} and Zhu \textit{et al.}\textsuperscript{20} measured the isotherms of isobutane in silicalite-1 and reported a step at four molecules per unit cell. This observation is in good agreement with the results simulated by CBMC simulations. The adsorption properties of n-hexane in silicalite-1 have extensively been studied, and there are a lot of the isotherm data in open literature\textsuperscript{2-3, 21-25} available. However, the adsorption of the branched alkanes has received much less attention. The reported isotherms of the branched isomers were only measured at relatively high temperatures and low pressures and did not show a two-step adsorption behavior predicted by the molecular simulations.
This chapter presents the isotherm data of \( n \)-hexane, 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane in silicalite-1, determined by the TEOM technique.\(^2\) A volume filling process with two different spaces is used to interpret the adsorption. A dual-site Langmuir expression is used to describe the isotherm data. In addition, the thermodynamic properties such as adsorption enthalpy and entropy are derived to characterize interactions between adsorptive and adsorbent.

### 4.2 Experimental

A Rupprecht & Patashnick TEOM 1500 mass analyzer (100 mg sample volume) was used in an experimental set-up designed for measurements of equilibrium, transient adsorption, and desorption on microporous materials. A detailed description of the TEOM operating principles is given in chapter 1 of this thesis, and the validity of the TEOM technique to accurately measure isotherm data has been verified in chapter 2.

Based on the operating principles, the TEOM yields information about mass changes rather than absolute sample masses. The total mass change measured consists of the amount adsorbed and the mass change caused by the change of the gas density in the tapered sample tube. The change in the gas density depends on the type of gas and the operating conditions. To correct for the mass change caused by the change in the density of the gas phase, reference experiments have to be performed. As mentioned in chapter 1, the relationship between the mass change in the reference runs and the partial pressure of an adsorbing gas is almost linear. If equilibrium adsorption for strong adsorptives is operated at very low partial pressures, this mass change caused by the density change in the gas phase will become negligible.

The silicalite-1 crystals with a ratio Si/Al > 1300 were synthesized in-house. The detailed physical properties of the sample are presented in chapter 2 of this thesis.

Prior to the experiments the crystals were outgassed in the following way. After a temperature rise with a rate of 10 K min\(^{-1}\) \textit{in situ} in a helium flow rate of 200 cm\(^3\) (NTP) min\(^{-1}\) (NTP: room temperature and 101.3 kPa), the sample was heated at 573 K for 12 hours in order to remove adsorbed impurities.

Helium was obtained as an ultra-high purity gas (>99.999%). The liquid adsorptives such as \( n \)-hexane, 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane were obtained from Alfa Aesar or Aldrich, with specified purities over 99%, and were used without further purification.

The isotherm data were measured in the temperature range from 303 to 408 K for \( n \)-hexane, 2-methylpentane, 3-methylpentane and from 303 to 473 K for 2,3-dimethylbutane. At least four temperatures were used for each adsorptive to reduce the uncertainty in the derived thermodynamic properties. Most experiments were duplicated, and both adsorption and desorption experiments were performed to confirm reversibility.
4.3 Results and Discussion

4.3.1 Isotherms
Experimental adsorption data for linear and branched C\textsubscript{8} alkanes in silicalite-1 are given in Figures 4-1 to 4-4. The measured isotherm data for NC6 at 303 K have a constant value of eight molecules per unit cell, see Figure 4-1. For the single branched alkanes, a two-step adsorption behavior can be clearly seen in Figures 4-2 and 4-3. In addition, both single branched alkanes show very similar adsorption trends. It is interesting to note constant isotherm data measured with a value of four molecules per unit cell for 23DMB at 303 K and at the pressure range investigated, presented in Figure 4-4.

**Isotherm model.** The adsorption of n-hexane (NC6) in the MFI zeolites has been extensively studied by both experiments and molecular simulation techniques. Generally speaking, the isotherm data obtained by both methods are consistent. The determined saturation amount...
adsorbed of NC6 in silicalite-1 is about eight molecules per unit cell. The experimental data of the maximum loading, reported in literature and measured in this study, for NC6 are summarized in Table 4-1. The agreement can be considered to be very good.

Molecular simulations suggest the occurrence of a kind of phase transition in the adsorption of NC6 in silicalite-1.\textsuperscript{28} It is shown that NC6 molecules first take an ordering arrangement in the zigzag channels before loadings above approximately half the maximum loading (four molecules per unit cell) can be reached. Due to the additional loss of entropy, an increased pressure is needed to “freeze” the molecules in the channels. This increase in pressure is reflected as a step in the adsorption isotherms. Van Well \textit{et al.}\textsuperscript{18} and Millot \textit{et al.}\textsuperscript{29} have proposed that there are two distinct adsorption sites in silicalite-1 for NC6 available, based on temperature-programmed desorption results.

For single branched alkanes 2-methylpentane (2MP) and 3-methylpentane (3MP) in silicalite-1, the CBMC simulations have confirmed that these molecules prefer to reside in the channel intersections but can also occupy the channel space, resulting in a two-step adsorption
behavior. Figure 4-5 shows a comparison of 2MP isotherm data in this study with the data from the simulation. Some deviations between experiment and simulation can be seen, but reasonably both results agree and show a two step adsorption behavior. Experimentally, the equilibrium adsorption data of 2MP and 3MP have to be measured at relatively low pressures. The measured maximum loadings for these two single branched alkanes, from literature and this study, are listed in Table 4-1.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>T (K)</th>
<th>p (kPa)</th>
<th>q_{\text{max}} (m.u.c.)</th>
<th>Ref.</th>
</tr>
</thead>
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<td>1.313</td>
<td>8.27</td>
<td>Sun et al. 3</td>
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<td></td>
<td>295</td>
<td>2</td>
<td>7.79</td>
<td>Arbuckle et al. 25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.11</td>
<td>Yang et al. 24</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>6.29</td>
<td>8.11</td>
<td>this study</td>
</tr>
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<td>2MP</td>
<td>373</td>
<td>2</td>
<td>3.89</td>
<td>Cavalcante et al. 30</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>2</td>
<td>5.03</td>
<td>Arbuckle et al. 25</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>6.40</td>
<td>5.21</td>
<td>this study</td>
</tr>
<tr>
<td>3MP</td>
<td>373</td>
<td>2</td>
<td>4.36</td>
<td>Cavalcante et al. 30</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>2</td>
<td>5.64</td>
<td>Arbuckle et al. 25</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>6.32</td>
<td>5.79</td>
<td>this study</td>
</tr>
<tr>
<td>23DMB</td>
<td>383</td>
<td>3.33</td>
<td>2.85</td>
<td>Cavalcante et al. 30</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>6.35</td>
<td>4.08</td>
<td>this study</td>
</tr>
</tbody>
</table>

*a Molecules per unit cell.
For 2,3-dimethylbutane (23DMB) adsorption in silicalite-1, only the isotherm data at 383, 423, and 473 K are reported in literature. The measured maximum loadings from the literature and this study are included in Table 4-1.

Theories of adsorption on heterogeneous surfaces or sites are usually based on the concept of independent sites or patches, so that the total amount adsorbed is simply a summation over the various parts:

\[ q(T, p) = \sum_i q_i(T, p, E_i) \]  (4-1)

\( q_i(T, p, E_i) \) is called the local adsorption isotherm with energy of adsorption (\( E_i \)) at site i. \( q(T, p) \) is the overall single-component isotherm measured experimentally. If one assumes that the local adsorption isotherm is given by the Langmuir model, the total adsorption isotherm for the bimodal two-site discrete distribution in eqn. (4-1) can be expressed

\[ q = q_A^{\text{sat}} \frac{K_A p}{1 + K_A p} + q_B^{\text{sat}} \frac{K_B p}{1 + K_B p} \]  (4-2)

where \( q_A^{\text{sat}} \) and \( K_A \) are the saturation capacity and the affinity parameter or equilibrium constant on the first set of sites, respectively, and \( q_B^{\text{sat}} \) and \( K_B \) are the analogous parameters on the second set of sites. By convention, we assume that the first set of sites has the larger affinity parameter, i.e., \( K_A > K_B \).

Following the concept in chapter 3, the saturation capacities in the two sets of sites are prior defined for the adsorption of linear and branched C₆ isomers in silicalite-1. Richards and Rees\(^{21}\) proposed that the saturation amount could be split into the numbers of molecules located in two representative adsorption sites. \( q_A^{\text{sat}} \) and \( q_B^{\text{sat}} \) have the same value of four molecules per unit cell, based on the length of the channels and of the intersections as well as on the adsorptive molecular size. The number, four molecules per unit cell, is called the "magic" number by Olson and Reischman,\(^{32}\) because it represents the number of intersections, the number of straight channels, and the number of zigzag channels per unit cell in silicalite-1. Thus a four-parameter isotherm model in eqn. (4-2) is simplified to a two-parameter isotherm one as follows

\[ q = 4 \frac{K_A p}{1 + K_A p} + 4 \frac{K_B p}{1 + K_B p} \]  (4-3)

The combined fitting by the above DSL isotherm model is given by the solid lines for NC6, 2MP, and 3MP in Figures 4-1 to 4-3. For 23DMB, the experimentally adsorbed amounts did not indicate a distinction between channels and intersections (Figure 4-4). The measured amount adsorbed is almost independent of the pressure investigated at 303 K, and these determined isotherm data have the same value of four molecules per unit cell, which is equal to that of the theoretical value in the intersections. Therefore, a simple Langmuir expression was used with the intersection adsorption capacity for fitting the isotherms at 303-473 K for 23DMB/silicalite-1 system, also shown in Figure 4-4.

\[ q = 4 \frac{K_A p}{1 + K_A p} \]  (4-4)
For the other adsorbents higher loadings were obtained. For NC6 the observed capacity was in agreement with the theoretical value.

The estimated values of the adsorption equilibrium constants for each temperature, $K_A$ and $K_B$, are listed in Table 4-2 for all the systems studied. These values were obtained by nonlinear regression of the experimental data on either the DSL model or the Langmuir isotherm using the fixed values of the saturation loadings.

**n-Hexane.** The isotherms for NC6, shown in Figure 4-1, indicate that small kinks are present at about four molecules per unit cell at the temperature range 338-373 K. This observation is in agreement with the results from Richard and Rees$^{21}$, Eder$^{33}$, and Yang and Rees$^{24}$. A comparison of the isotherm data with the literature data is shown in Figure 4-6. These results agree well with the experimental data from Yang and Rees$^{24}$ and the simulation data from Vlugt et al.$^{11}$ However, significant deviations from the results reported by Sun et al.$^{3}$ can be clearly seen in Figure 4-6. The reason for these deviations is uncertain, but it might be pointed out that the data from Sun et al.$^{3}$ at higher temperatures are too low. So, the work of Yang and Rees$^{24}$ seems to be the most reliable source for comparison.

The idea of intracrystalline molecular rearrangement of adsorbing species has been developed by Micke et al.$^{34}$ for the system of NC6/MFI structure, based on both geometrical constraints and differences in the interaction potential topology between the straight channels and zigzag channels with the intersections within the MFI crystals. The NC6 molecules sitting in the zigzag channels have less mobility, compared to those residing in the straight channels with the intersections.$^{34}$ From the CBMC simulations, Smit et al.$^{28,35}$ also observed a small two-step adsorption behavior at four molecules per unit cell for n-hexane in silicalite-1. The molecular length of n-hexane is about 1.03 nm,$^{21}$ which is much longer than the straight channel length only (0.46 nm$^{21}$). Therefore n-hexane molecules cannot be wholly located in the straight channel segments and they share with the intersections. At lower loadings the hexane molecules move freely in the channels through the intersections. If a fraction of the intersections is occupied (four segments per unit cell), other adsorbing molecules cannot

![Figure 4-6 Comparison of NC6 isotherm data with data from the literature. (●) This study at 373 K, (▲) data from Yang and Rees$^{24}$ at 373 K, (●) data from Sun et al.$^{3}$ at 374 K and (▼)CBMC-simulation data from Vlugt et al.$^{11}$ at 373 K.](image-url)
reside in the straight channels at the same time. At high pressures, almost all adsorbing molecules fit exactly in the zigzag channels with a length of 0.66 nm.\(^{21}\) They no longer move freely and keep their noses and tails out of the intersection. In such a configuration the whole channels and the intersections can now be tightly packed with NC6 molecules. This may explain the small ‘kink’ in the adsorption isotherm; to fill the entire zeolite structure neatly, the hexane molecules located in the zigzag channels have to be frozen in these channels.\(^{28}\) This “freezing” of the positions of the NC6 molecules implies a loss of entropy and therefore will occur only if the pressure (or gas phase chemical potential) is sufficiently high to compensate for this loss.

Table 4-2 Estimated values of adsorption equilibrium constants and standard deviation of fit by combined fitting of isotherm data [eqns. (4-3) and (4-4)]

| \(T\) (K) | \(q^\text{sat}_A\) (m.u.c.) | \(K_A\) (kPa\(^{-1}\)) | \(q^\text{sat}_B\) (m.u.c.) | \(K_B\) (kPa\(^{-1}\)) | \(\sigma_{\text{model}}\) | \\
|-------|---------|---------|---------|---------|---------| \\
| NC6:  |         |         |         |         |         | \\
| 303   | 4       | 2730    | 4       | 80.8    | 0.163   | \\
| 338   | 4       | 171     | 4       | 4.02    |         | \\
| 358   | 4       | 44.8    | 4       | 9.42 \times 10^{-1} |         | \\
| 373   | 4       | 18.0    | 4       | 3.51 \times 10^{-1} |         | \\
| 388   | 4       | 7.77    | 4       | 1.41 \times 10^{-1} |         | \\
| 408   | 4       | 2.79    | 4       | 4.66 \times 10^{-2} |         | \\
| 2MP:  |         |         |         |         |         | 0.137   | \\
| 303   | 4       | 760     | 4       | 8.09 \times 10^{-2} |         | \\
| 338   | 4       | 66.7    | 4       | 5.66 \times 10^{-3} |         | \\
| 373   | 4       | 9.25    | 4       | 6.53 \times 10^{-4} |         | \\
| 408   | 4       | 1.80    | 4       | 1.09 \times 10^{-4} |         | \\
| 3MP:  |         |         |         |         |         | 0.119   | \\
| 303   | 4       | 726     | 4       | 1.31 \times 10^{-1} |         | \\
| 338   | 4       | 62.0    | 4       | 8.83 \times 10^{-3} |         | \\
| 373   | 4       | 8.40    | 4       | 9.88 \times 10^{-4} |         | \\
| 408   | 4       | 1.60    | 4       | 1.61 \times 10^{-4} |         | \\
| 23DMB\(^c\): |         |         |         |         |         | 0.075   | \\
| 303   | 4       | 352     |         |         |         | \\
| 408   | 4       | 0.606   |         |         |         | \\
| 423   | 4       | 0.316   |         |         |         | \\
| 438   | 4       | 0.172   |         |         |         | \\
| 453   | 4       | 0.0979  |         |         |         | \\
| 473   | 4       | 0.0515  |         |         |         | \\

\(^a\) Molecules (unit cell)\(^{-1}\). \(^b\) Standard deviation model. \(^c\) Fitted by a single Langmuir expression [eqn. (4-4)].
The configurational-entropic effects lead to adsorption heterogeneity. At loadings below four molecules per unit cell, NC6 molecules can sit in either the straight or the zigzag channels with the intersections. Globally, at these conditions a homogeneous adsorption site is considered, designed as site A. However, at loadings over four molecules per unit cell, the adsorption of the adsorbing molecules “frozen” in the zigzag channels will be energetically different. This gives rise to a pseudo-second-adsorption site, designed as site B. NC6 isotherm data are well described by the DSL model over the temperature and pressure range studied, as shown in Figure 4-1.

**Single branched alkanes.** For 2MP and 3MP in silicalite-1, a step is clearly observed for the isotherm at 303 K. At pressures below 1 kPa, the measured isotherm data are almost constant and have a value of four molecules per unit cell. At pressures above 1 kPa, the amount adsorbed starts to increase with increasing pressure. Also at 338 K the measured isotherm data do not change with pressure significantly and they have a close value of four molecules per unit cell. Only at 373 and 408 K the isotherms are of “type-I” (in Brunauer’s classification).

Compared to *n*-hexane much less experimental data are reported on the adsorption of branched alkanes in silicalite-1. Adsorption isotherms have been reported for various hexane isomers by Cavalcante and Ruthven and for 2MP and 3MP by Arbuckle *et al.* Comparisons of the isotherms at 373 K with the literature data are also shown in Figures 4-2 and 4-3. At higher pressures of 2MP the reported isotherm data in this study are in good agreement with the results from Cavalcante and Ruthven, but the data in this study are higher at low pressures. The agreement can be considered to be satisfactory for 3MP in the whole pressure range investigated.

2MP and 3MP show a very similar adsorption behavior, although the amount adsorbed for 3MP is slightly higher than that for 2MP under the same conditions. This observation is in agreement with that from Cavalcante and Ruthven. Probably, 3MP is a less asymmetric molecule, compared to 2MP, and can pack in silicalite-1 more efficiently, since the thermodynamic properties (see below) are quite similar.

A two-step adsorption behavior is more pronounced for the single branched alkanes, compared to NC6. A preferential packing of four molecules per unit cell for the single branched molecules corresponds to the number of the intersections per unit cell in silicalite-1. For a loading above the saturation amount in the intersections the adsorbing molecules are forced at higher pressures into the channels. The DSL model, eqn. (4-3), implicitly describes this behavior; the intersections are filled first, followed by the channels. So, this stepwise adsorption behavior has a different cause, compared with NC6.

**2,3-Dimethylbutane.** Only very limited adsorption data have been reported for 23DMB in silicalite-1. Cavalcante and Ruthven and Voogd and Van Bekkum reported the isotherms at high temperatures. Reasonable agreement with the data from Cavalcante and Ruthven is found. Figure 4-4 shows this comparison for 23DMB at 423 K. Unfortunately, a two-step adsorption behavior for 23DMB in silicalite-1 has not been observed due to the experimental limitation that higher loadings could not be determined.
4.3.2 Thermodynamic properties

The affinity parameters, $K_A$ and $K_B$, quantify the adsorption interaction of a given adsorbive with an adsorbent. The magnitude of $K_A$ and $K_B$ depends on both the properties of the adsorptive and of the adsorbent, and corresponding to the affinity of the adsorbive for the adsorbent. From the fitted $K_A$ and $K_B$, the adsorption enthalpies and entropies can be obtained via the Van't Hoff equation, eqn. (4-5)

$$K_i = \exp \left( \frac{\Delta S_i^{\text{ads}}}{R} \right) \exp \left( \frac{-\Delta H_i^{\text{ads}}}{RT} \right)$$

where $\Delta H_i^{\text{ads}}$ and $\Delta S_i^{\text{ads}}$ are the adsorption enthalpy and entropy, respectively. The ln $K_A$ and ln $K_B$ as a function of $1/T$ are shown graphically in Figures 4-7 and 4-8, respectively. The linearity of these plots indicates that meaningful thermodynamic parameters result from the DSL model for NC6, 2MP, and 3MP and from the Langmuir model for 23DMB. The derived values of the adsorption enthalpy and entropy are listed in Table 4-3.

![Figure 4-7 ln $K_A$ as a function of $1/T$ for the adsorption of the linear and branched C₆ isomers in site A of silicalite-1. (●) NC6, (▲) 2MP, (○) 3MP and (▼) 23DMB.](image)

![Figure 4-8 ln $K_B$ as a function of $1/T$ for the adsorption of the linear and branched C₆ isomers in site B of silicalite-1. (●) NC6, (▲) 2MP and (○) 3MP.](image)
Table 4-3 Estimated adsorption enthalpy and -entropy values for linear and branched C₆ isomers in silicalite-1 for the combined fitting of the isotherm adsorption data

<table>
<thead>
<tr>
<th>Adsorbive</th>
<th>$-\Delta H_{A}^{ads}$</th>
<th>$-\Delta H_{B}^{ads}$</th>
<th>$-\Delta S_{A}^{ads}$</th>
<th>$-\Delta S_{B}^{ads}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC6</td>
<td>67.4 ± 3.6$^a$</td>
<td>73.0 ± 1.9$^a$</td>
<td>148 ± 9$^a$</td>
<td>196 ± 5$^a$</td>
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<tr>
<td>2MP</td>
<td>59.2 ± 1.5</td>
<td>64.7 ± 13.3</td>
<td>131 ± 4</td>
<td>226 ± 45</td>
</tr>
<tr>
<td>3MP</td>
<td>59.9 ± 1.5</td>
<td>65.6 ± 2.2</td>
<td>135 ± 4</td>
<td>225 ± 12</td>
</tr>
<tr>
<td>23DMB</td>
<td>62.2 ± 1.7</td>
<td></td>
<td>148 ± 4</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ 95% confidence error.

Table 4-4 Adsorption enthalpy and -entropy values for linear and branched C₆ isomers in silicalite-1 given by literature$^a$

<table>
<thead>
<tr>
<th>Adsorbive</th>
<th>$-\Delta H^{ads}$</th>
<th>$-\Delta S^{ads}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ mol$^{-1}$</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>NC6</td>
<td>71 [2], 70 [3], 62$^b$ to 84$^c$ [21], 69.8$^b$ to 82$^c$ [22], 84 [36], 72 [37], 82 [38], 70 [39], 71.8$^d$ and 78.2$^e$ [17]</td>
<td>128 [37], 153 [38], 85 [40], 121.8$^{d,ed}$ and 187.6$^e$ [17]</td>
</tr>
<tr>
<td>2MP</td>
<td>61.5$^d$ [17], 62.7 [30], 63 [41]</td>
<td>116$^d$ [17]</td>
</tr>
<tr>
<td>3MP</td>
<td>66.8$^{d,ed}$ and 70.5$^e$ [16], 67.7 [30], 63 [41]</td>
<td>110$^{d,ed}$ and 202$^e$ [16]</td>
</tr>
<tr>
<td>23DMB</td>
<td>54.3 [30]</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Reference numbers are in brackets. $^b$ Infinite diluted concentration in the zeolite. $^c$ Saturation of the zeolite. $^d$ Adsorption site A. $^e$ Adsorption site B.

An overview of the reported adsorption enthalpies in literature for linear and branched C₆ isomers in silicalite-1 is presented in Table 4-4. For NC6 in silicalite-1, the determined value of the adsorption enthalpy covers a wide range, as seen in Table 4-4. However, most of the reported adsorption enthalpies for NC6 in silicalite-1 are about -70 kJ mol$^{-1}$. The literature enthalpy data are mostly related to adsorption techniques at low loadings and for NC6 they should therefore be compared with the adsorption enthalpy in site A. The present result is considered to be satisfactory.

Only Cavalcante and Ruthven$^{30}$ reported the adsorption enthalpies for 2MP and 3MP in silicalite-1, derived from the isotherms. The absolute values of the adsorption enthalpy in this study are slightly lower than those by Cavalcante and Ruthven$^{30}$, especially for 3MP. There is a difference of 5 kJ mol$^{-1}$ in the adsorption enthalpy between 2MP and 3MP from Cavalcante and Ruthven’s results. However, this study shows only minor differences in the adsorption
enthalpy for both types of sites between two single branched C₆ alkanes. This result is supported by molecular simulations by June et al., as indicated in Table 4-4. Differences in the adsorbed amounts of 2MP and 3MP are only ascribed to differences in packing efficiency.

For 23DMB, the absolute value of the adsorption enthalpy in this study is about 8 kJ mol⁻¹ higher than the data from Cavalcante and Ruthven. The reason is not clear. In view of the intersectional space, two branched-end groups in 23DMB molecule can reside in the intersection, which leads to a more confined packing, compared to one branched-end in the intersection for 2MP and 3MP. Consequently, the interactions between the two branched-end groups and the intersection wall are enhanced and may increase the adsorption enthalpy, compared to 2MP and 3MP. Indeed the results in this study show that the absolute value of the adsorption enthalpy for 23DMB is slightly higher than that for 2MP and 3MP. The confined packing of 23DMB in the intersection means an additional loss of entropy. From the adsorption entropy values in Table 4-3, it is also found that 23DMB molecules have less degrees of freedom than the single branched isomers in the intersections.

Millot et al. have reported the adsorption enthalpy and entropy for NC6, 2MP, and 3MP, by temperature-programmed desorption (TPD), in which equilibrium conditions are maintained. The TPD curves show two peaks for all NC6, 2MP, and 3MP in silicalite-1. From those, the authors defined two types of adsorption sites for the adsorptives. These reference data are also included in Table 4-4. The present results have the same trend as that reported by Millot et al.: the absolute values of the adsorption enthalpy and entropy in site B are higher than those in site A. It is worth noting that the data in this study are in fair agreement with those obtained by temperature-programmed desorption. It is logical that the absolute value of the adsorption enthalpy for the single branched isomers in site B is higher than in site A. Due to low-energy bending of the O-Si-O angle, which leads to some flexibility in the channel dimensions of silicalite-1, the branched-end group has a confined packing in the channels. This results in enhancing the interactions between adsorptive and the channel wall.

From the derived values of thermodynamic properties for the two "sites", it can be concluded that the difference in the adsorption enthalpy between two types of adsorption sites is relatively small, compared to the significant difference in the adsorption entropy for NC6. One can also recall the thermodynamic Gibbs free energy, associated with the adsorption equilibrium constants, K_A and K_B.

\[ \Delta G_i^{\text{ads}} = \Delta H_i^{\text{ads}} - T \Delta S_i^{\text{ads}} \]  

(4-6)

Weaker adsorption in the range from four to eight molecules per unit cell means that \( \Delta G_i^{\text{ads}} \) is less negative than \( \Delta G_i^{\text{ads}} \). According to the results in Table 4-3, \( \Delta H_i^{\text{ads}} \) becomes more negative, increasing somewhat in magnitude; this would make \( \Delta G_i^{\text{ads}} \) more negative, leading to stronger adsorption. Since the adsorption is actually weaker by definition (\( K_B < K_A \)), \( - T \Delta S_i^{\text{ads}} \) must be more positive. This implies a more ordered state for the last four molecules of NC6, 2MP, and 3MP relative to adsorption in site A. Since for NC6 no real distinctly different adsorption locations are present in silicalite-1 structure, the adsorption in the DSL
form is artificial. It merely reflects a change in ordering of the molecules above four molecules per unit cell, the so-called commensurate freezing.\textsuperscript{28}

Compared to \textit{n}-hexane in silicalite-1, the difference between the adsorption entropies in the two sites is more pronounced for the single branched C\textsubscript{6} alkanes. The molecular size of the single branched alkanes, with a kinetic diameter of 0.5 nm,\textsuperscript{43} is comparable to the diameters of the channels. On the other hand, there is more space to accommodate the branched-end group in the intersections. Thus it can be expected that the loss of entropy will be more significant if the single branched C\textsubscript{6} molecules are adsorbed in the smaller channels. The CBMC simulations indeed show that there is a striking difference in the probability distribution of single branched alkanes between adsorption locations in the channels and in the intersections. At loadings below four molecules per unit cell, the branched molecules only reside in the intersections due to the entropic effects.\textsuperscript{10-11, 14}

The loss of the adsorption entropy for the single branched C\textsubscript{6} molecules residing in the channels is more than that for \textit{n}-hexane. This also indicates that \textit{n}-hexane has a higher packing efficiency than the branched alkanes within the silicalite-1 structure. Thus these entropic effects might be applied to the separation of linear and branched C\textsubscript{6} isomers by silicalite-1 adsorbents or membranes.\textsuperscript{44} The initial filling of the channels by \textit{n}-hexane and the intersections by the branched alkane molecules will consequently not be independent processes due to the spatial phenomena, and non-ideal behavior is expected. Unfortunately, the mixture isotherm data are rarely available, because the experimental determination of such isotherms is significantly more complicated and time-consuming than the measurements for the pure components. The mixture isomers of NC\textsubscript{6} and 2MP, determined by the CBMC simulations,\textsuperscript{12} show a curious maximum in the loading of 2MP; this loading decreases to almost zero with increasing pressure due to the entropic effects that the adsorbed 2MP molecules can be squeezed out by \textit{n}-hexane at higher pressures, since packing efficiency is much higher for NC6 within the silicalite-1 structure. This leads to high adsorption selectivity for \textit{n}-hexane. Recently reported permeation data for NC6 and 2MP mixture by a silicalite-1 membrane support this concept.\textsuperscript{5}

### 4.4 Conclusions

Adsorption isotherms for linear and branched C\textsubscript{6} alkanes in silicalite-1 were accurately measured with the novel TEOM technique at multiple temperatures. A two-step adsorption behavior is observed for 2-methylpentane and 3-methylpentane at four molecules per unit cell of silicalite-1. This observation is in agreement with that predicted by CBMC simulations. A small "kink" in the isotherm at about four molecules per unit cell is present for \textit{n}-hexane adsorption. For 2,3-dimethylbutane, the measured maximum loading is limited to four molecules per unit cell under the conditions investigated. The Langmuir model with the fixed saturation capacity in the intersections appropriately describes the isotherm data of 2,3-dimethylbutane.

The adsorption was interpreted in terms of a volume filling process with two different types of spaces for 2-methylpentane and 3-methylpentane and with two different energetic
configurations for \(n\)-hexane. This can be described by a dual-site Langmuir expression. The derived thermodynamic properties like the enthalpies and entropies associated with adsorption in two adsorption sites are physically sound and, in good agreement with the literature data as far as available. The observed two-step adsorption behavior for single branched \(C_6\) isomers in silicalite-1 is attributed to the large difference in the adsorption entropy between the molecular locations in the intersections and in the channels. Normal hexane has a higher packing efficiency than the branched \(C_6\) alkanes within the silicalite-1 structure. The credibility of the proposed approach is enhanced by its ability to provide meaningful thermodynamic properties.

References

26 Chapter 1 of this thesis.
Diffusion of Linear and Branched C\textsubscript{6} Alkanes in Silicalite-1

The kinetic patterns of adsorption and desorption have been studied for linear and branched C\textsubscript{6} alkanes in silicalite-1 of uniform shape and size by the TEOM technique. Unlike the conventional gravimetric method, the TEOM technique minimizes external mass and heat transfer limitations in transient experiments due to a high flow rate of the carrier gas through the sample bed without affecting measurements. Model equations, in which the thermodynamic (correction) factor for intracrystalline diffusivities has been taken into account, enable the determination of diffusivities from adsorption and desorption patterns operated in the non-linear adsorption range and bypass simplifying assumptions for analytic solutions. The determined diffusivities at zero coverage for the studied adsorptives, which cover three orders of magnitude (10^-12-10^-15 m\textsuperscript{2} s\textsuperscript{-1}), are in good agreement with those available by zero-length column (ZLC) and chromatography methods so far. It is shown that the TEOM technique can be easily used not only for steady state and equilibrium measurements, but also for transient uptake and desorption experiments.

This chapter is based on the following publication:
5.1 Introduction

The measurement of micropore diffusion in zeolite crystals and other microporous solids has proven a far more challenging task than might have been anticipated.\textsuperscript{12} The developments of microscopic techniques such as the pulsed-field-gradient nuclear-magnetic resonance (PFG-NMR)\textsuperscript{3,4} and quasi-elastic neutron scattering (QENS)\textsuperscript{5} methods for measuring self-diffusion under equilibrium conditions have proven to be a major milestone. For many experimental systems, diffusivities yielded by the microscopic measurements are several orders of magnitude larger than the values derived from traditional macroscopic measurements. Most of the more obvious explanations of these remarkable discrepancies between determined diffusivities by the microscopic and macroscopic techniques have been considered and shown to be inapplicable.\textsuperscript{2} The application of the microscopic methods is expected to have a significant progress on the study of adsorption kinetics. However, such an application has been limited by the short relaxation times of many adsorbed molecules. Inherently, macroscopic techniques are still being developed and widely used for measuring diffusivities in microporous materials.

The macroscopic methods involve measurement of an aggregate property such as pressure, temperature, or concentration. Some well-known macroscopic techniques are uptake,\textsuperscript{6,7} frequency response (FR),\textsuperscript{8,9} and gas chromatographic method,\textsuperscript{10-11} including the zero-length-column (ZLC) technique.\textsuperscript{12} Most recently, Talu \textit{et al.}\textsuperscript{13} developed a technique that measures the diffusive flux through a single-crystal membrane (SCM) to determine micropore diffusivities under steady-state conditions. A brief review on the various macroscopic techniques can be found in literature.\textsuperscript{13-15}

The development of most of the macroscopic techniques has been focused on eliminating the intrusion of thermal effects and external resistances to mass transfer in transient measurements of adsorption/desorption rates. The commonly used ZLC technique can be considered either as the limiting case of a chromatographic experiment for a very short column or as the limiting case of a desorption rate measurement in a flow system in order to minimize such problems.\textsuperscript{1} But in the ZLC technique the composition of the gas mixture must be accurately known. The accurate determination of the concentrations may become critical for low concentrations at long desorption times and the ZLC is mainly applied in the linear adsorption range.

Recently, a technique, the so-called tapered element oscillating microbalance (TEOM),\textsuperscript{16} has been developed. The main feature of the TEOM technique is an oscillating element that is based on inertial instead of gravimetric forces, to measure the mass change in the sample bed with a good time resolution and stability. A well-defined gas phase can be easily achieved due to a high flow rate of the carrier gas through the adsorbent bed. Compared with conventional thermobalances, this improves the external mass and heat transfer for microporous materials and also results in a fast response to gas-phase changes.

Since Rupprecht and Patashnick invented the TEOM 1500 series analyzer, some work associated with this technique has been reported. For instance, simultaneous measurements of adsorption, reaction, and coke information were investigated by Hershkowitz and Madiera\textsuperscript{17},
Chen et al.\textsuperscript{18-21}, and Liu et al.\textsuperscript{22} Rekoske and Barteau\textsuperscript{23} and Petkovic and Larsen\textsuperscript{24} used this technique to investigate catalytic kinetics. Equilibrium adsorption properties of microporous materials have been carried out by Zhu et al.\textsuperscript{16, 25-27} Only Rebo et al.\textsuperscript{28} used the TEOM technique to measure the diffusivities of toluene, o-xylene, and p-xylene in HZSM-5 zeolite.

The present study is undertaken on the diffusion of n-hexane, 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane in silicalite-1 crystals with a uniform shape and size, illustrating the application of the TEOM technique for determining intracrystalline diffusivities. Since in general zeolithic diffusion phenomena are strongly concentration dependent, a solution of the diffusion equation including the appropriate functional dependency on adsorptive concentration is proposed in order to interpret correctly the adsorption or desorption curves performed in the non-linear adsorption range. In addition, the determined diffusivities are compared with those by other macroscopic techniques such as ZLC, FR, membrane permeation, and conventional gravimetric methods to demonstrate the applicability of the TEOM method.

5.2 Experimental

5.2.1 Apparatus
A Rupprecht & Patashnick TEOM 1500 mass analyzer (100 mg sample volume) was used for measurements of transient adsorption and desorption in silicalite-1. A detailed description of the TEOM operating principles is given in chapter 1 of this thesis. The used set-up is schematically shown in Figure 1-5 of chapter 1.

5.2.2 Materials
The silicalite-1 crystals used were the same as those described in chapter 2. The silicalite-1 crystals had a uniform shape and size of about $120 \times 50 \times 50 \, \mu m \ (L \times H \times W)$, as determined by SEM, shown in Figure 2-2 in chapter 2.

The purity for helium and all the used liquid adsorptives has been presented in chapter 4.

5.2.3 Procedure

![Figure 5-1 Schematic of the TEOM sample bed.](image)

The usual pattern followed in these experiments was to regenerate a given adsorbent sample and then carry out an adsorption-desorption cycle, with continuous monitoring of the mass changes. The oscillating microbalance was connected through a data acquisition board to a personal computer, with data acquisition software LabView. The microbalance measurements were accurate to 1 \mu g.

The sample bed was loaded with a thin layer of the silicalite-1 crystals, which weights were
Figure 5-2 System pressure and mass change responses during initial flow transients for 3MP in silicalite-1 (20.4 mg) at 373 K. He flow rate: 100 cm³ (NTP) min⁻¹ and 3MP liquid flow rate: 0.1 g h⁻¹. 

(a) System pressure response and (b) mass change.

about 10 to 20 mg. This minimized the quantity of sample required for diffusivity measurements. Quartz wool was used at the top and the bottom of the sample bed to keep the adsorbent particles firmly packed, which was essential for a stable measurement. The partial pressure of the feed vapor was determined by its fraction of the total feed rate through the sample bed and the total pressure. A mixture of helium and sample vapor was used. The flow rates of helium were in the range from 100 to 200 cm³ (NTP) min⁻¹ (NTP: room temperature and 101.3 kPa). A schematic of the sample bed is shown in Figure 5-1.

Prior to the experiments the silicalite-1 crystals were outgassed by heating at 573 K in a helium flow rate of 200 cm³ (NTP) min⁻¹ for 12 hours in order to remove adsorbed impurities. The absence of contamination during this procedure was indicated by absence of a sample mass change. Thereafter, the sample was allowed to cool under helium carrier to the desired temperature for the adsorption experiments. An adsorption run was initiated by replacing the helium stream by a predetermined mixture of helium and the sample vapor. The feed was maintained until the sample was equilibrated as indicated by constant mass change. Desorption was then carried out by changing helium with the feed gas to pure helium and running until the sample mass change returned to its initial value.
Due to a high flow rate through the sample bed, changing the total flow rate would cause a change in the system pressure. Therefore, nearly constant flows were always maintained for either uptake or desorption experiments. This essentially minimized the experimental errors caused by the system pressure change. Figure 5-2 shows an example of the transient operation of 3-methylpentane in silicalite-1 at 373 K. The carrier gas with a flow rate of 100 cm\(^3\) (NTP) min\(^{-1}\) was controlled by a mass flow controller (MFC2) to the sample bed, see Figure 1-5 in chapter 1. At these conditions the pressure indicator was 110 kPa, also shown in Figure 5-2 a. The mass change measured was negligible, indicated in Figure 5-2 b. This served as a base line. Then the carrier gas flow was switched off during the adsorption stage of the experiment. Simultaneously, the liquid carrier gas (He) with a flow rate of 100 cm\(^3\) (NTP) min\(^{-1}\) (MFC5) and 2MP liquid with a flow rate of 0.1 g h\(^{-1}\) (LMFC) were introduced to the sample bed through the “CEM” unit. It took about 5 to 10 s for this operation to introduce a mixture of helium and the adsorptive vapor to the sample bed and maintain constant system pressure. Figures 5-2 a and b show the system pressure response and the corresponding mass change during this operation. Thus the measured data of the mass changes might be contaminated by these initial flow transients during the first 5-10 s and uptake or desorption curves were corrected for that effect, i.e. the data points in the first 5-10 s were not used until the mass signal increased above the original level. A graph of the fraction of the amount adsorbed or desorbed as a function of time was then constructed directly from points on the recorded data file after a correction was made for the effect of the initial flow transients. The TEOM 1500 analyzer can store current data in up to three data files with different time intervals simultaneously. For fast adsorption or desorption processes, a data file with a storage interval of 0.84 s was used, while the file with an interval of either 10 s or 60 s was used for slow processes.

5.3 Engineering Model

Adsorption and desorption by the zeolitic crystals with a uniform shape and size may be described by a particle diffusion model which assumes:

1. Micropore diffusion within the zeolitic crystals is the rate controlling process.
2. Diffusion is described by Fick's law with a concentration-dependent diffusivity, which may be expressed by Darken’s equation.\(^{14}\)
3. Instantaneous adsorption equilibrium is maintained at the exterior crystal surface.
4. The void space and the sample bed are taken as a well-mixed reservoir, thus ignoring concentration variations in the spatial direction (also see Appendix B).
5. An ideal gas behavior of adsorptive in the void space and constant total flow through the sample bed.

This model pictures the adsorption process as a rapid equilibrium of adsorbed molecules on the crystal surface with the surrounding gas phase, followed by slow diffusion of the adsorbed molecules to the interior of crystal. This process continues until the crystal is uniformly equilibrated with the gas phase composition. Desorption is pictured as the exact reverse of this
process, with the adsorbed phase concentration at the crystal surface in equilibrium with the desorbed adsorptive concentration in flowing He stream.

Based on the above assumptions, a mass balance equation over the void space yields the following partial differential equation (PDE) system.

\[
\frac{dp}{dt} = \frac{p_m - p}{\varepsilon_b f_b} + \left( \frac{1 - \varepsilon_b}{\varepsilon_b} \right) a' R_e T \left[ \left( D(q) \frac{\partial q}{\partial r} \right) \right]_{r=R_e}
\]

where \( p \) is the partial pressure of adsorptive in the void space, \( p_m \) the partial pressure in the inlet, \( q \) the amount adsorbed, \( \varepsilon_b \) the sample bed porosity, \( R_p \) the radius of the crystal, \( a' \) the interfacial area per unit volume of adsorbent, \( R_e \) the universal gas constant, \( T \) the temperature, and \( D(q) \) the concentration-dependent diffusivity. The last term on the RHS of eqn. (5-1) represents the flux through the external surface into or out of the particles. \( t_b \) is a residence time, defined as

\[
t_b = \frac{V_b}{\Phi_v}
\]

where \( V_b \) is the sample bed volume and \( \Phi_v \) the total flow rate through the sample bed. By assuming cylindrical particles (see Appendix C), the solid-phase mass balance may be expressed as

\[
\frac{\partial q}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[ D(q) r \frac{\partial q}{\partial r} \right]
\]

The boundary conditions for the particle are

\[
q|_{r=R_p} = q(p); \quad \frac{\partial q}{\partial r}|_{r=0} = 0
\]

where \( q(p) \) in molecules per unit cell represents either the dual-site Langmuir (DSL) isotherm for \( n \)-hexane, 2-methylpentane, and 3-methylpentane

\[
q = 4 \frac{K_A p}{1 + K_A p} + 4 \frac{K_B p}{1 + K_B p}
\]

or the Langmuir model for 2,3-dimethylpentane,\(^{29}\)

\[
q = 4 \frac{K_A p}{1 + K_A p}
\]

where \( K_A \) and \( K_B \) represent the adsorption equilibrium constants. The factor 4 represents the saturation loading for the adsorption location, in molecules per unit cell (m.u.c.). The concentration dependency of the diffusivity is described by a thermodynamic factor, for a single adsorbent corresponding with Darken’s equation.\(^{14}\)

\[
D(q) = D_0 \left( \frac{\partial \ln p}{\partial \ln q} \right) = D_0 \Gamma
\]

where \( D_0 \) is the diffusivity at infinite dilution. The thermodynamic factor \( \Gamma \) can be determined from the adsorption isotherms. For the DSL model, the thermodynamic factor can be expressed by eqn. (5-7) (see Appendix A).
\[ \Gamma = q \left( \frac{C_1}{C_2} + \frac{1}{8 - q} \right) \]  

(5-7)

with

\[ C_1 = (K_A + K_B) - \frac{(4 - q)(K_A - K_B)^2}{\sqrt{(4 - q)^2 (K_A - K_B)^2 + 64K_A K_B}} \]  

(5-8a)

\[ C_2 = (q - 4)(K_A + K_B) + \sqrt{(4 - q)^2 (K_A - K_B)^2 + 64K_A K_B} \]  

(5-8b)

For the Langmuir model,

\[ \Gamma = \frac{q}{4 - q} \]  

(5-9)

For a low loading \( \Gamma \) approaches one. The mathematical model is fully formulated once the initial conditions are defined. For a step change in adsorptive partial pressure from zero to \( p_0 \) (adsorption) or from \( p_0 \) to zero (desorption) at time \( t = 0 \), the appropriate initial conditions are

\[ q|_{t=0} = 0 \] for adsorption  

(5-10a)

\[ q|_{t=0} = q_0 \] for desorption  

(5-10b)

For convenience the following dimensionless variables and parameters are defined:

\[ X = \frac{r}{R_p}; \quad Y = \frac{p}{p_0}; \quad Q = \frac{q}{q_0} \]  

(5-11)

The mass balance eqn. (5-1) becomes

\[ \frac{dY}{dt} = \frac{1-Y}{\varepsilon_b} + \left( \frac{1-\varepsilon_b}{\varepsilon_b} \right) \left( \frac{q_0}{p_0} \right) \left( \frac{a' D_0 R_p T}{R_p} \right) \left( \Gamma \frac{\partial Q}{\partial X} \right)_{X=1} \] for adsorption  

(5-12a)

\[ \frac{dY}{dt} = \frac{-Y}{\varepsilon_b} + \left( \frac{1-\varepsilon_b}{\varepsilon_b} \right) \left( \frac{q_0}{p_0} \right) \left( \frac{a' D_0 R_p T}{R_p} \right) \left( \Gamma \frac{\partial Q}{\partial X} \right)_{X=1} \] for desorption  

(5-12b)

The balance equation over a cylindrical crystal can be expressed:

\[ \frac{\partial Q}{\partial t} = \frac{D_0}{R_p^2} \left( \Gamma \frac{\partial Q}{\partial X} + \frac{\partial \Gamma}{\partial X} \frac{\partial Q}{\partial X} + \frac{\partial^2 Q}{\partial X^2} \right) \]  

(5-13)

The boundary conditions for the particle are

\[ Q|_{X=1} = Q(Y); \quad \frac{\partial Q}{\partial X}|_{X=0} = 0 \]  

(5-14)

where \( Q(Y) \) is the isotherm in a dimensionless form. \( Q|_{X=1} \) evolves to one (adsorption) or to zero (desorption), depending on how fast the gas phase concentration \( Y \) reaches its final value in the CSTR. The initial conditions are

\[ Q|_{t=0} = 0 \] for adsorption  

(5-15a)

\[ Q|_{t=0} = 1 \] for desorption  

(5-15b)

In transient experiments the model describes the behavior of the concentrations of adsorptive in the gas phase and in the adsorbent crystals as a function of time and space. The determination of the only unknown parameter, i.e. the intracrystalline diffusivity \( D_0 \) for zero
loading, is based on the method of the least squares. The non-linear least squares method consists of minimizing the sum of the squared difference (residual) between the data predicted by the model \(Q^{\text{cal}}\) and the experimental data \(Q^{\text{obs}}\). This difference is called the sum of squares of residuals (SSR) and is given by

\[
\text{SSR} = \sum_{n=1}^{N_c} w_n (Q^{\text{obs}}_n - Q^{\text{cal}}_n)^2
\]  

(5-16)

where \(n\) is the observation number, \(N_c\) the total number of observations, and \(w_n\) the weighing factor of the \(n\)-th observation. The weighing factor may be used when not all the data have the same significance. Since this is usually not the case or unknown the weighing factor is normally taken as one for every observation.

Starting with an initial guess of the diffusivity, the minimization of the SSR is achieved by varying the parameter according to the Simplex or the Levenberg-Marquardt method until a minimum is encountered and convergence criteria have been reached. For each parameter iteration step the PDE solver is called, which is based on the method of lines and the sparse ordinary-differential-equation solver LSODES. From the variance-covariance matrix, confidence intervals for the parameter estimates are calculated. Both models with and without thermodynamic factor \(\Gamma\) were considered.

### 5.4 Results and Discussion

The diffusivities of \(n\)-hexane (NC6), 2-methylpentane (2MP), 3-methylpentane (3MP), and 2,3-dimethylpentane (23DMB) in silicate-1 were measured at multiple temperatures. The intracrystalline diffusivities \(D_0\) fitted by governing equations (5-12b) and (5-13) from desorption curves are listed in Table 5-1. For all fits the 95% confidence error is less than 1%. Figure 5-3 shows fitting examples for the desorption of NC6 at temperatures 338–408 K. Generally speaking, the current model describes desorption curves very well. For all fits, the sample bed porosity \(\varepsilon_b\) and the radius of the crystal \(R_p\) used were 0.4 and \(2.07 \times 10^{-4}\) m, respectively. Table 5-1 also includes the experimental conditions such as the initial partial pressure \(p_0\), the corresponding loading \(q_0\), the carrier gas flow rate \(\Phi_v\), and the adsorbent amount \(W\).

#### 5.4.1 Adsorption versus desorption

It is often observed that uptake curves for physical adsorption have the same rates as those for corresponding desorption modes in the linear adsorption range. Indeed, the current observation shows the same feature, illustrated in Figure 5-4. For 23DMB, which has a low occupancy in silicate-1 at higher temperatures, the fitted diffusivities from both uptake and desorption curves are consistent. Therefore, in the linear adsorption range, the adsorption and desorption response curves coincide. In addition, there is only a minor difference between the estimated diffusivities of the models including \(\Gamma\) and without \(\Gamma\). Consequently, at a low partial pressure upon adsorption or a low initial loading upon desorption, the absolute values of the rates are equal for both adsorption and desorption.
Figure 5-3 Rates of desorption for NC6 in silicalite-1 in flowing He with a rate of 200 cm$^3$ (NTP) min$^{-1}$. Lines are the model fits and (O) experimental data. (a) 338 K and $q_0 = 5.25$ m.u.c. (molecules per unit cell); (b) 358 K and $q_0 = 4.90$ m.u.c.; (c) 373 K and $q_0 = 3.27$ m.u.c.; (d) 388 K and $q_0 = 3.27$ m.u.c.; (e) 408 K and $q_0 = 2.36$ m.u.c.

In contrast, for a strong adsorptive, even at a very low partial pressure the linear adsorption range is exceeded and the uptake rate is much higher than the corresponding desorption rate. Figure 5-5 represents the rates of the adsorption and desorption for 3MP in silicalite-1 at 303 K and 0.45 kPa in the first 400 s. The absolute rate for adsorption is about one magnitude higher than for desorption in the initial stage. This behavior is fully caused by non-linearity in the adsorption isotherm, and an asymmetry develops between adsorption and desorption. In addition, temperature changes inside the crystals may occur, which are proportional to the adsorption or desorption rate. So, in this nonlinear adsorption range the heat effects upon adsorption are more pronounced than upon desorption. The isothermal conditions are then easier maintained for the desorption mode. Therefore, in this study most diffusivities were extracted from desorption curves.
Table 5-1 Estimated diffusivities at zero coverage in silicalite-1 for the adsorptives studied

<table>
<thead>
<tr>
<th>Adsorptive</th>
<th>$T$ (K)</th>
<th>$p_0$ (kPa)</th>
<th>$q_0$ (m.u. $^b$)</th>
<th>$\Phi_V$ (cm$^3$ min$^{-1}$)</th>
<th>$W$ (mg)</th>
<th>$D_0$ (m$^2$ s$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>NC6</td>
<td>338</td>
<td>0.17</td>
<td>5.25</td>
<td>200</td>
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<tr>
<td></td>
<td>358</td>
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<td>4.90</td>
<td>200</td>
<td>9.9</td>
<td>4.32 $\times 10^{-13}$</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>0.17</td>
<td>3.27</td>
<td>200</td>
<td>9.9</td>
<td>7.63 $\times 10^{-13}$</td>
</tr>
<tr>
<td></td>
<td>388</td>
<td>0.18</td>
<td>2.51</td>
<td>200</td>
<td>9.9</td>
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</tr>
<tr>
<td></td>
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<td>2.88</td>
<td>200</td>
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<td>1.30 $\times 10^{-12}$</td>
</tr>
<tr>
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<td>1.40 $\times 10^{-12}$</td>
</tr>
<tr>
<td></td>
<td>408</td>
<td>0.47</td>
<td>2.36</td>
<td>200</td>
<td>20.4</td>
<td>2.21 $\times 10^{-12}$</td>
</tr>
<tr>
<td>2MP</td>
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</tr>
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</tr>
<tr>
<td></td>
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<td>0.21</td>
<td>1.10</td>
<td>200</td>
<td>19.1</td>
<td>1.16 $\times 10^{-12}$</td>
</tr>
<tr>
<td></td>
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<td>1.72</td>
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<td>1.04 $\times 10^{-12}$</td>
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<td>408</td>
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<td>1.91 $\times 10^{-15}$</td>
</tr>
<tr>
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<td>3.96</td>
<td>100</td>
<td>20.4</td>
<td>2.49 $\times 10^{-14}$</td>
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<td>3.19</td>
<td>100</td>
<td>20.4</td>
<td>1.30 $\times 10^{-13}$</td>
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<tr>
<td></td>
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<td>100</td>
<td>20.4</td>
<td>4.57 $\times 10^{-13}$</td>
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<td>4.20 $\times 10^{-13}$</td>
</tr>
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<td>3.65</td>
<td>200</td>
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<td>4.71 $\times 10^{-13}$</td>
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<td>20.4</td>
<td>1.20 $\times 10^{-14}$</td>
</tr>
<tr>
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<td>2.33</td>
<td>100</td>
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<td>1.23 $\times 10^{-14}$</td>
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<td>423</td>
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<td>1.69</td>
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<td>438</td>
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<td>100</td>
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<td></td>
<td>438</td>
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<td>0.79</td>
<td>100</td>
<td>20.4</td>
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<tr>
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<tr>
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<tr>
<td></td>
<td>473</td>
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<td>0.36</td>
<td>100</td>
<td>20.4</td>
<td>1.44 $\times 10^{-13}$</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>2.38</td>
<td>0.44</td>
<td>100</td>
<td>9.9</td>
<td>1.53 $\times 10^{-13}$</td>
</tr>
</tbody>
</table>

$^a$ At room temperature and 101.3 kPa. $^b$ Molecules per unit cell.
Figure 5-4 Rates of adsorption and desorption for 23DMB in silicalite-1 (9.9 mg) in flowing He with a rate of 100 cm$^3$ (NTP) min$^{-1}$ at 453 K. (A) Adsorption data at an inlet partial pressure of 2.32 Pa, corresponding with the equilibrium amount adsorbed of 0.74 m.u.c.; (V) desorption data at an initial loading of 0.74 m.u.c. Lines are the fits; $D_0 = 8.20 \times 10^{-14}$ m$^2$ s$^{-1}$ (adsorption) and $D_0 = 8.74 \times 10^{-14}$ m$^2$ s$^{-1}$ (desorption).

Figure 5-5 Rates of adsorption and desorption for 3MP in silicalite-1 (20.4 mg) in flowing He with a rate of 100 cm$^3$ (NTP) min$^{-1}$ at 303 K in the first 400 s. (▲) Adsorption at an inlet partial pressure of 0.45 kPa; (▼) desorption at a corresponding initial loading of 4.21 m.u.c.

5.4.2 Thermodynamic factor
For the adsorption of NC6, 2MP, and 3MP in silicalite-1 the isotherm exhibits a two-step adsorption behavior, which can be described by the DSL model, while the isotherm of 23DMB can be described by the Langmuir model under the conditions investigated. The two-step behavior in the isotherm is due to the preferential location of molecules at certain sites in the silicalite-1 structure. Krishna et al. have proposed that this two-step adsorption behavior affects diffusion through the thermodynamic factor $\Gamma$.

In general, if uptake and/or desorption curves are measured in the non-linear adsorption range, the assumption of constant diffusivity might be a poor approximation for the micropore-diffusion controlled system. Due to the non-linearity of the equilibrium isotherm, the concentration-dependent diffusivity can be derived by eqn. (5-6). The thermodynamic
Chapter 5

Figure 5-6 Thermodynamic factor as a function of loading calculated from the isotherms.\(^9\) (a) NC6 at 388 K; (b) 2MP at 408 K; (c) 3MP at 408 K; (d) 23DMB at 408 K. Symbols indicate starting loadings used in desorption experiments at corresponding temperatures. (○) NC6; (▲) 2MP; (●) 3MP; (▼) 23DMB.

The thermodynamic factor \(\Gamma\) for the DSL model shows two extremes: a maximum at the first saturation point (four molecules per unit cell) and a minimum at a loading between four and eight molecules per unit cell. For the Langmuir model, the thermodynamic factor monotonously increases with increasing loading. These behaviors are illustrated in Figure 5-6 for the adsorptives studied. The maximum value of \(\Gamma\) at the first saturation point for the DSL model increases with increasing the ratio of \(K_A\) to \(K_B\), see eqn. (5-17). For NC6, this maximum peak is insignificant due to only a small "kink" in the isotherm at four molecules per unit cell, whereas it is pronounced for the single branched alkanes.

\[
\Gamma_{b=0.5} = 1 + \frac{1}{2} \left[ \left( \frac{K_A}{K_B} \right)^{\frac{1}{2}} + \left( \frac{K_A}{K_B} \right)^{-\frac{1}{2}} \right]
\]  

(5-17)

where \(\theta = 0.5\) corresponds to a loading of four molecules per unit cell. In Figure 5-6 are also indicated the starting loadings in the various desorption experiments to illustrate the range covered.

The importance of the thermodynamic factor on the diffusion behavior is illustrated by fitting results from the desorption curves of 3MP at different initial loadings in Figure 5-7. The model including \(\Gamma\) can appropriately describe the desorption patterns and the fitted \(D_0\) values are seen to be practically constant. However, the model with constant \(\Gamma\) does not match the desorption curves properly. In addition, the estimated values of the diffusivities change significantly with initial loading.

5.4.3 Comparison with literature data

\(n\)-Hexane. Diffusivity data at multiple temperatures obtained for NC6 in silicalite-1 are summarized in Table 5-1. Representative desorption curves are shown in Figure 5-3 for particular conditions of temperature, initial loading, and He flow rate. The theoretical curves, fitted according to eqns. (5-12a) and (5-13), are also shown; these are evidently in good agreement with the experimental data. The fitted diffusivity at zero coverage is almost
Figure 5-7 Comparison of the models with $\Gamma$ (solid line) and without $\Gamma$ (dashed line) for 3MP desorption data (O) at 408 K. (a) 100 cm$^3$ (NTP) min$^{-1}$ and $q_0 = 2.33$ m.u.c., $D_0 = 4.57 \times 10^{-13}$ m$^2$ s$^{-1}$ (with $\Gamma$) and $D_0 = 5.86 \times 10^{-13}$ m$^2$ s$^{-1}$ (without $\Gamma$); (b) 200 cm$^3$ (NTP) min$^{-1}$ and $q_0 = 3.66$ m.u.c., $D_0 = 4.71 \times 10^{-13}$ m$^2$ s$^{-1}$ (with $\Gamma$) and $D_0 = 7.09 \times 10^{-13}$ m$^2$ s$^{-1}$ (without $\Gamma$).

independent of initial loading and the results at 388 K (see Table 5-1) give an example. This also confirms the followed approach.

Plotting the diffusivities $D_0$ versus the inverse of the absolute temperature (Figure 5-8), a straight line is observed, following Arrhenius’ law:

$$D_0 = D_{0,\infty} \exp \left( \frac{-E_a}{R_g T} \right)$$  \hspace{1cm} (5-18)

where $E_a$ is the diffusional activation energy. Its value, estimated from the slope of the plot, is approximately 38 kJ mol$^{-1}$. A comparison with experimental data from other techniques is shown in Table 5-2.

Measurements for NC6 diffusion in MFI-type zeolites have been extensively carried out by means of different techniques. In general, there are vast unexplained differences between macroscopic and microscopic methods. The techniques used to determine intracrystalline diffusivities have been reviewed by Talu et al.$^{13}$ and Kärger and Ruthven$^{14}$, and most recently by Ruthven.$^{2}$ A comparison of the current data with those from other macroscopic techniques.
is also presented in Figure 5-8. The current results are in good agreement with the data determined by the ZLC and chromatography techniques.\textsuperscript{33-34} Compared with the data from the FR technique,\textsuperscript{35} agreement can be considered to be acceptable. Millot \textit{et al.}\textsuperscript{36} and Talu \textit{et al.}\textsuperscript{13} used the membrane permeation technique to measure NC6 diffusivities in silicalite-1. Both reported data were quite consistent, although Millot \textit{et al.}\textsuperscript{36} used a layer of intergrown crystals while Talu \textit{et al.}\textsuperscript{13} used a single crystal for determining the diffusivities. The diffusivities in the membrane permeation are higher by one order of magnitude. The membrane permeation technique for measuring micropore diffusivities was based on direct measurements of steady-state flux through a single zeolite crystal in a membrane arrangement.\textsuperscript{13} It was pointed out that the technique used was to measure directional diffusivity in the z-direction, while other macroscopic methods are for a combined effective diffusivity.\textsuperscript{13} In addition, using a layer of intergrown crystals in the membrane permeation technique, there is an uncertainty in the absolute value of the diffusivity, which is largely determined by the estimation of the effective membrane thickness.\textsuperscript{42} This is an explanation for the high values reported for the membrane permeation techniques; and more in general, for the discrepancy in diffusivity values in literature. The absolute value of the diffusivity is proportional to the square of the particle size used.

The reported value of the diffusional activation energy varies from 8 to 39 kJ mol\textsuperscript{-1} in literature. In general, the diffusional activation energy from microscopic techniques is much lower than that from macroscopic methods. Table 5-2 shows a comparison with literature data derived from the diffusivities determined by the macroscopic techniques. The current result is in good agreement with the results from Millot \textit{et al.}\textsuperscript{36} (membrane permeation), Jama \textit{et al.}\textsuperscript{34} (chromatography), and Bülow \textit{et al.}\textsuperscript{35} (FR) but higher than that determined by the ZLC technique.\textsuperscript{33} It should be taken into account that the value reported by Voogd \textit{et al.}\textsuperscript{33} was determined using two data points only, and therefore might have a somewhat higher experimental uncertainty. The work of Jama \textit{et al.}\textsuperscript{34} seems to be the most reliable source for comparison.
Table 5-2 Comparison of the activation energies of diffusion

<table>
<thead>
<tr>
<th>Adsorptive</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>Technique</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC6</td>
<td>25.0</td>
<td>ZLC</td>
<td>Voogd et al.$^{35}$</td>
</tr>
<tr>
<td></td>
<td>36.0</td>
<td>Chromatography</td>
<td>Jama et al.$^{34}$</td>
</tr>
<tr>
<td></td>
<td>39.0$^a$</td>
<td>FR</td>
<td>Bülow et al.$^{35}$</td>
</tr>
<tr>
<td></td>
<td>34.7</td>
<td>Membrane permeation</td>
<td>Millot et al.$^{36}$</td>
</tr>
<tr>
<td></td>
<td>38.1</td>
<td>TEOM</td>
<td>this study</td>
</tr>
<tr>
<td>2MP</td>
<td>35.0</td>
<td>Gravimetry</td>
<td>Xiao and Wei$^{37}$</td>
</tr>
<tr>
<td></td>
<td>46.0</td>
<td>Gravimetry</td>
<td>Cavalcante and Ruthven$^{38}$</td>
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<td>TAP</td>
<td>Keipert and Baerns$^{39}$</td>
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<td>Gravimetry</td>
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<td>TEOM</td>
<td>this study</td>
</tr>
</tbody>
</table>

$^a$ Value derived from the reported $D_0$ data.

**Single branched alkanes.** Microscopic methods are especially suitable for fast-diffusing species. The lowest diffusivities that these methods can measure are in the order of $10^{-9}$-$10^{-11}$ m$^2$ s$^{-1}$. To my knowledge, up to now there have been very few data concerning diffusivities

![Graph](image.png)

Figure 5-9 In $D_0$ as a function of $1/T$ for 2MP in silicalite-1. (●) This study; (△) gravimetry, from Cavalcante and Ruthven$^{38}$; (○) gravimetry, from Xiao and Wei$^{37}$; (▼) TEX-PEP, from Schumacher et al.$^{40}$; (◆) TAP, from Keipert and Baerns$^{38}$. 

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of branched C₆ alkanes in silicalite-1, determined by microscopic techniques. In a previous chapter it was pointed out that the position of the methyl group affects the packing efficiency in the silicalite-1 structure. Here, the effect of the methyl group location in the main chain on the diffusivity was investigated.

The determined diffusivities at zero coverage for 2MP and 3MP are summarized in Table 5-1. Values of $D_0$ were plotted as a function of the inverse of the temperature. A straight linear dependence is found for 2MP and 3MP in Figures 5-9 and 5-10, respectively. The values of the diffusional activation energy are summarized in Table 5-2. The $D_0$ value for 2MP is almost twice as that for 3MP. Also there is a lower diffusional activation energy (see Table 5-2) for 2MP. This observation is in agreement with that from Cavalcante and Ruthven. The reason may be explained by the longer tail in the 2MP molecule, providing a somewhat more favorable orientation for the molecule through the silicalite-1 channels as compared to 3MP. But it has been found that a symmetrical 3MP molecule has a higher packing efficiency inside silicalite-1. So, there is a difference in the effect of the position of the methyl group in the main chain between adsorption and diffusion.

The reported literature data of diffusivities are also included in Figures 5-9 and 5-10. The current data are in good agreement with those determined by other techniques so far. Especially, the values of 3MP diffusivities are in excellent agreement with those by the ZLC. For 2MP, the value of the diffusional activation energy agrees with the data from Cavalcante and Ruthven but is higher than determined by either the transient analysis of products (TAP) or the tracer-exchange experiments with positron emission profiling (TEX PEP), see Table 5-2. But the diffusivity data in the overlapping temperature range correspond well. Good agreement with literature data is found for 3MP.
2,3-Dimethylbutane. The experiments were performed for 23DMB at temperatures 408–473 K. The determined diffusivities at zero coverage are included in Table 5-1. As expected, the diffusivity values for the double- branched alkane are much lower than those for the single- branched compounds, due to the increased steric constraint caused by addition of one more methyl group to the main alkane chain. A value of 63.9 kJ mol⁻¹ for the diffusional activation energy is found; this value is very close to the heat of adsorption (62.2 kJ mol⁻¹).²⁹ The critical diameter of 23DMB is around 0.58 nm.³⁸ This dimension, being so close to the silicalite-1 pore openings, strongly affects the diffusion process through the channels.

A comparison of the data in this study with literature values is shown in Figure 5-11. Diffusivities are in good agreement with those determined by the ZLC method, but some deviations from those by either volumetric or gravimetric methods can be seen. It might be pointed out that the presence of the heat effects and bed diffusion resistances is suspected in volumetric and gravimetric experiments. The derived diffusional activation energy is only slightly higher compared to literature data, but it can be also considered to be satisfactory.

![Figure 5-11](image)

Figure 5-11 $D_0$ as a function of $1/T$ for 23DMB in silicalite-1. (★) This study; (▲) ZLC, from Cavalcante and Ruthven⁴⁸; (●) volumetry, from Voogd and Van Bekkum⁴¹; (▼) gravimetry, from Xiao and Wei⁴⁷.

5.4.4 Heat effects

An adsorption/desorption process is known to release heat upon adsorption or absorb energy upon desorption. Heats of adsorption of the investigated $C_6$ alkanes in silicalite-1 range from 60 to 70 kJ mol⁻¹,²⁹ and such a magnitude can cause a significant change in the temperature of the silicalite-1 crystals if the dissipation of energy to the surrounding is not fast enough. Therefore, the crystal temperature increase (adsorption) or decrease (desorption) depends on the interplay between the rate of heat release due to adsorption or heat absorption due to desorption and the dissipation rate of energy to the surrounding. Since the thermal conductivity of silicalite-1 crystals is greater than that of the gas (helium) surrounding the crystals, the temperature within the crystals can be assumed uniform and all the heat transfer resistance is in the gas film surrounding the crystal. This is called the lumped thermal model.¹⁵
When the heat released by the adsorption process can not be dissipated fast enough into the surrounding, the temperature of the crystals will change. To study the effects of heat transfer on the uptake behavior, one needs to solve mass balance equations (5-1) and (5-3) together with the following lumped thermal model for heat balance around the crystal:\(^{15}\)

\[
\frac{dT}{dt} = \left( -\Delta H^\text{ads} \right) \left( -a'D_0\Gamma \frac{\partial q}{\partial r} \right)_{r=R_s} - a'h_T (T - T_b)
\]  

(5-19)

In obtaining the heat balance equation, one assumes that the heat resistance by conduction inside the crystal is insignificant compared to the heat resistance outside the crystal, which is described by the second term in the RHS of eqn. (5-19). This is, in general, the case for packed catalyst beds. Because of such an assumption, the temperature inside the crystal is uniform. The first term in the RHS of eqn. (5-19) is the amount of heat released per unit volume per unit time. \(\Delta H^\text{ads}\) represents the adsorption enthalpy, \(\bar{\rho}_p C_{p,p}\) the mean heat capacity per unit volume of the crystal, and \(T_b\) the surrounding temperature. \(h_T\) is the heat transfer coefficient, which can be described by the following correlation for packed beds\(^{33}\)

\[
h_T = \frac{\lambda_f}{2R_p} \left( 2 + 1.1 \Re_p^{0.6} \Pr^{1/3} \right) = \frac{\lambda_f}{2R_p} \left[ 2 + 1.1 \left( \frac{2R_p \eta_f}{\eta_f} \right)^{0.6} \left( \frac{C_{p,f} \eta_f}{\lambda_f} \right)^{1/3} \right]
\]  

(5-20)

where \(\Re_p\) is the particle Reynolds number, \(\Pr\) the Prandtl number, \(\lambda_f\) the fluid thermal conductivity, \(\eta_f\) the fluid viscosity, \(\rho_f\) the fluid density, \(C_{p,f}\) the fluid heat capacity, and \(u\) the superficial fluid velocity.

**Table 5-3 Physical constants of helium and the silicalite-1 crystal at the temperatures investigated**

<table>
<thead>
<tr>
<th>T (K)</th>
<th>(\lambda_f) (J m(^{-1}) s(^{-1}) K(^{-1}))</th>
<th>(\rho_f) (kg m(^{-3}))</th>
<th>(\eta_f) (kg m(^{-1}) s(^{-1}))</th>
<th>(C_{p,f}) (J kg(^{-1}) K(^{-1}))</th>
<th>(\bar{\rho}<em>p C</em>{p,p}) (J m(^{-3}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>1.51 \times 10(^{-5})</td>
<td>0.161</td>
<td>1.94 \times 10(^{-5})</td>
<td>5.20 \times 10(^3)</td>
<td>1.28 \times 10(^6)</td>
</tr>
<tr>
<td>338</td>
<td>1.61 \times 10(^{-5})</td>
<td>0.144</td>
<td>2.09 \times 10(^{-5})</td>
<td>5.20 \times 10(^3)</td>
<td>1.38 \times 10(^6)</td>
</tr>
<tr>
<td>358</td>
<td>1.67 \times 10(^{-5})</td>
<td>0.136</td>
<td>2.17 \times 10(^{-5})</td>
<td>5.20 \times 10(^3)</td>
<td>1.44 \times 10(^6)</td>
</tr>
<tr>
<td>373</td>
<td>1.71 \times 10(^{-5})</td>
<td>0.131</td>
<td>2.23 \times 10(^{-5})</td>
<td>5.20 \times 10(^3)</td>
<td>1.48 \times 10(^6)</td>
</tr>
<tr>
<td>388</td>
<td>1.76 \times 10(^{-5})</td>
<td>0.126</td>
<td>2.29 \times 10(^{-5})</td>
<td>5.20 \times 10(^3)</td>
<td>1.52 \times 10(^6)</td>
</tr>
<tr>
<td>408</td>
<td>1.82 \times 10(^{-5})</td>
<td>0.119</td>
<td>2.37 \times 10(^{-5})</td>
<td>5.20 \times 10(^3)</td>
<td>1.57 \times 10(^6)</td>
</tr>
<tr>
<td>423</td>
<td>1.86 \times 10(^{-5})</td>
<td>0.115</td>
<td>2.43 \times 10(^{-5})</td>
<td>5.20 \times 10(^3)</td>
<td>1.60 \times 10(^6)</td>
</tr>
<tr>
<td>438</td>
<td>1.91 \times 10(^{-5})</td>
<td>0.111</td>
<td>2.49 \times 10(^{-5})</td>
<td>5.20 \times 10(^3)</td>
<td>1.64 \times 10(^6)</td>
</tr>
<tr>
<td>453</td>
<td>1.95 \times 10(^{-5})</td>
<td>0.108</td>
<td>2.55 \times 10(^{-5})</td>
<td>5.20 \times 10(^3)</td>
<td>1.67 \times 10(^6)</td>
</tr>
<tr>
<td>473</td>
<td>2.01 \times 10(^{-5})</td>
<td>0.103</td>
<td>2.62 \times 10(^{-5})</td>
<td>5.20 \times 10(^3)</td>
<td>1.72 \times 10(^6)</td>
</tr>
</tbody>
</table>

\(^a\) Extrapolated data from reference 44. \(^b\) Calculated from the ideal gas law. \(^c\) Data from reference 45. \(^d\) Data of SiO\(_2\) heat capacity from reference 45 and density of the silicalite-1 crystal of 1760 kg m\(^{-3}\).
The values of physical properties from literature data are listed in Table 5-3. In the last two decades, the physical properties of MFI-type zeolites have been intensively investigated. However, to my knowledge, no data on the thermal conductivity and heat capacity of silicalite-1 were available in open literature. Therefore it was assumed that the heat capacity on a mass basis of silicalite-1 was similar as for pure SiO₂.

Apparently, the estimated heat-transfer coefficient, the mean heat capacity of the silicalite-1 crystal, and the corrected diffusivity are a function of temperature. As an approximation, it is assumed that these physical parameters are constant in the simulations of uptake and/or desorption rates inside the silicalite-1 crystals. The desorption rate increases with increasing the initial loading, diffusivity, and concentration gradient at the surface of the crystal. At the same initial loading, the desorption rate is mainly determined by the diffusivity. The heat effects are proportional to the heat of adsorption and the adsorption or desorption rate, while these effects can be minimized by increasing the carrier gas flow rate, which results in enhancing the heat transfer rate. Figure 5-12 shows the temperature change ($T - T₀$) in the first 100 s for unfavorable cases with the strongest heat effects upon desorption for each adsorptive. The input parameters for these simulations are included in Table 5-4.

### Table 5-4 Input parameter values in the simulations of temperature changes shown in Figure 5-12

<table>
<thead>
<tr>
<th>Adsorptive</th>
<th>$T₀$</th>
<th>$p₀$</th>
<th>$u$</th>
<th>$hₖ$</th>
<th>$D₀$</th>
<th>$-\Delta H^{ads}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
<td>kPa</td>
<td>m s⁻¹</td>
<td>J m⁻² s⁻¹</td>
<td>m² s⁻¹</td>
<td>kJ mol⁻¹</td>
</tr>
<tr>
<td>NC₆</td>
<td>388</td>
<td>0.39</td>
<td>0.346</td>
<td>2.76</td>
<td>$1.40 \times 10^{-12}$</td>
<td>67.4</td>
</tr>
<tr>
<td>2MP</td>
<td>408</td>
<td>0.73</td>
<td>0.363</td>
<td>2.81</td>
<td>$9.87 \times 10^{-13}$</td>
<td>59.2</td>
</tr>
<tr>
<td>3MP</td>
<td>408</td>
<td>2.33</td>
<td>0.182</td>
<td>2.15</td>
<td>$4.20 \times 10^{-13}$</td>
<td>59.9</td>
</tr>
<tr>
<td>23DMB</td>
<td>408</td>
<td>6.44</td>
<td>0.182</td>
<td>2.15</td>
<td>$1.20 \times 10^{-14}$</td>
<td>62.2</td>
</tr>
</tbody>
</table>

As shown in Figure 5-12, the maximum temperature changes are within the initial 20 s for all the adsorptives. For NC₆, desorption curves investigated at the temperature range from 338 to 408 K, the maximum temperature changes inside the crystals are less than 7 K. For single branched alkanes 2MP and 3MP, the heat effects are less pronounced. In current approach the reported diffusivities (Table 5-1) were extracted by fitting desorption curves over the whole time span. The estimated diffusivities at zero coverage are almost constant under either different He flow rates or different sample amounts used, see Table 5-1. In addition, the same $D₀$ values were derived from the desorption curves without using the data points in the first 50 s. This also indicates that the heat effects, although present under the experimental conditions, are apparently not significant.
Figure 5-12 Simulated temperature changes in the first 100 s during desorption under the most unfavorable conditions. The input parameter values are presented in Table 5-4. (a) NC6; (b) 2MP; (c) 3MP; (d) 23DMB.

Figure 5-13 Deviation from the diffusivity at $T_b = 408$ K as a function of temperature change. (a) NC6; (b) 2MP; (c) 3MP; (d) 23DMB.

The temperature change during desorption for 23 DMB is below 1 K, and after 100 s the simulated temperature changes are less than 0.5 K. The fastest desorption experiment took about 3000 s at 473 K. So the heat effects can be considered to be nearly absent for 23 DMB desorption under the investigated conditions.

The experimental errors in the determined diffusivity, caused by the temperature change inside crystals, can also be evaluated by eqn. (5-19), based on the derived value of the diffusional activated energy, shown in Table 5-2. The deviation from the reference data, i.e. $D_0$ at $T_b$, as a function of temperature change is presented in Figure 5-13. For the most serious heat effects for NC6 at 408 K, the deviation is less than the 15% in the first 20 s. Since the diffusivity data were fitted on the desorption model over the whole time series, it can be expected that the experimental errors caused by the temperature change would be much less than the 15% for NC6, 10% for 2MP and 3MP, and 5% for 23DMB, as follows from Figure 5-13 for the maximum temperature change. These experimental errors can be considered to be acceptable for measurements of micropore diffusivities. In addition, it is mentioned that the
temperature effect not only affects the diffusivity but also the adsorption equilibrium constant, resulting in a reduction of the influence. This is beyond the scope of this thesis and will be presented elsewhere.

The ZLC method is commonly used to determine diffusivities in zeolites. Often the operation is performed in the linear adsorption range and the diffusivities or diffusion time constants can be fitted by simple analytic equations under certain assumptions for the initial or for the long time data. The latter approach is usually followed; this yields the linear relationship of the logarithm of concentration in a dimensionless form as a function of time. The operation in the linear adsorption range also indicates that the ZLC method is applicable only for weakly adsorbing systems. In addition, in the ZLC technique the composition of the gas mixture must be accurately determined from the desorption stream, which becomes critical for low concentrations at long desorption times, and just those data are used for the analysis. The TEOM technique measures the integral sample mass change with a good time resolution and stability. It can be easily used not only for steady state and equilibrium measurements, but also for transient uptake and desorption experiments. In the presented numerical approach the simplifying assumptions about gas phase concentrations and constant diffusivity are not required, but the proper relations are used. Therefore, the concentration dependency of diffusivities can be incorporated. This is easily extended to analyze data from simple variants of the stimulus response technique applied in the TEOM to study self-diffusion and counter-diffusion in binary systems.

5.5 Conclusions

Engineering models, in which the thermodynamic factor for intracrystalline diffusivities has been taken into account, enable the determination of micropore diffusivities from uptake and desorption curves operated outside the linear adsorption range and bypass simplifying assumptions for analytic solutions. The determined diffusivities at zero coverage for the studied adsorptives, which cover three orders of magnitude ($10^{12}$-$10^{15}$ m$^2$ s$^{-1}$), are in good agreement with those by zero-length column (ZLC) and chromatography methods so far. The $D_0$ value for 2-methylpentane is almost twice as that for 3-methylpentane. The diffusivity values for the double-branched molecule 2,3-dimethylbutane are much lower than those for the single-branched compounds, due to the increased steric constraint caused by addition of one more methyl group to the main alkane chain.

Unlike the conventional gravimetric method, the TEOM technique minimizes external mass and heat transfer limitations in transient experiments due to a high flow rate of the carrier gas through the sample bed without affecting measurements. The isothermal conditions are easier maintained for the desorption mode. The TEOM is comparable with the ZLC method. But the TEOM technique measures the integral sample mass change with a good time resolution and stability. It can be used not only for steady state and equilibrium measurements, but also for transient uptake and desorption experiments. Simple variants of the TEOM experiment allow the technique to be extended to the measurement of (tracer) self-diffusion and counter-diffusion in a binary system.
References

29. Chapter 4 of this thesis.
The adsorption of ethane, ethene, propane, propene, and unsaturated linear C4 molecules in the all-silica DD3R has been investigated using the TEOM technique. Single-component adsorption isotherms are reported at temperatures in the range from 303 to 473 K. At high temperatures, the Langmuir isotherm appropriately describes the equilibrium adsorption data for ethane, ethene, propene, trans-but-2-ene, and buta-1,3-diene in the all-silica DD3R. For the propene data below 340 K a dual-site Langmuir model was used. The analysis of thermodynamic properties, like the isosteric heat and entropy of adsorption, indicates that the adsorbent is energetically uniform. Only minor differences exist between the adsorption of ethane and ethene. Transient adsorption experiments reveal that the eight-ring windows of the all-silica DD3R are accessible to propene, trans-but-2-ene, and buta-1,3-diene molecules, while they exclude propane, cis-but-2-ene, and but-1-ene molecules. The high shape selectivity for propene and trans-but-2-ene suggests that the all-silica DD3R might be effective as a selective adsorbent for the separations of either propene and propane mixtures or but-2-ene mixtures.

This chapter is based on the following publications:
6.1 Introduction

Porous tectosilicates can be divided into two classes, clathrasil and zeolite, according to the classification proposed by Liebau and co-workers.\textsuperscript{1-2} The name "clathrasil" was first introduced by Gies \textit{et al.}\textsuperscript{3} for a class of porous tectosilicates. Clathrasils are clathrate compounds with 3-dimensional 4-connected host frameworks of silica containing cage-like voids between the [SiO$_4$] tetrahedra. Deca-dodecasils 3R (DD3R) is a member of the clathrasil family possessing topologically different frameworks. Gies\textsuperscript{4-5} did pioneering work on the synthesis and structural identification of the clathrasil DD3R.

The crystal structure of the clathrasil DD3R is built by corner-sharing [SiO$_4$] tetrahedra that are connected to pseudo-hexagonal layers of face-sharing pentagonal dodecahedra ([5$^{12}$] cages). These layers are stacked in a $ABCABC$ sequence and interconnected by additional [SiO$_4$] tetrahedra that form six-membered rings between the layers. Thus, two new types of cages arise, a small decahedron, [4$^{3}$5$^{6}$6$^{1}$] cage, and a large 19-hedron, [4$^{3}$5$^{12}$6$^{1}$8$^{3}$] cage, see Figure 6-1, the latter housing the 1-aminoadamantane template molecule during the synthesis. A detailed description of the clathrasil DD3R structure can be found in literature.\textsuperscript{4} On thermal treatment of the clathrasil DD3R up to \textit{ca.} 773 K the template molecules can be decomposed and the fragments are driven out of the cages, transforming the clathrasil to a phase possessing zeolitic properties.

An optimum procedure for the clathrasil DD3R crystallization that ensures the phase purity of DD3R has been developed by Den Exter.\textsuperscript{6} The synthesis was scaled up to batches of 20 grams. A complete removal of the template lead to the pure silica sample, referred to as all-

![Diagram of clathrasil DD3R structure](image)

Figure 6-1 Building units and framework of the DD3R. After Gies.\textsuperscript{4}
silica DD3R.

One unit cell of the all-silica DD3R has the chemical formula Si$_{120}$O$_{240}$, and consists of six decahedra, nine dodecahedra, and six 19-hedra. The silica host framework can completely be constructed by linking decahedra and dodecahedra through common faces. The interlayer six-membered rings with a maximum pore diameter of 0.28 nm expand the distance between two [5$^{12}$] layers and give rise to [4$^{3}$5$^{12}$6$^{1}$8$^{3}$] cavities. These cavities or cages are interconnected through eight-membered rings with a free cross diameter of about 0.45 nm. Thus a two-dimensional pore system is formed parallel to (001), with the cavities in a hexagonal arrangement, where each cavity is connected with three other cavities. The [4$^{3}$5$^{12}$6$^{1}$8$^{3}$] cavity has a free volume of about 0.35 nm$^3$ and a free cross diameter of 0.875 nm by assuming a sphere-like cage.

The adsorption of hydrocarbons in porous materials is an important subject that has received considerable attention in recent years. Apart from the traditional interest from the standpoint of separation, the understanding of adsorption, from a theoretical point of view, is of utmost importance. The size of the adsorptive molecule plays an important role because it will limit the range of pores and/or windows for which they are accessible. Matching the diameter of the pore aperture of microporous materials with the critical dimensions of gas molecules might lead to higher separation factors. Selectivity can be reached by differences in strength of adsorption or by steric hindrance of the molecule to be adsorbed in the pore system. Considering the critical diameters of small hydrocarbons, the all-silica DD3R with eight-ring windows might meet these requirements. Moreover, in heterogeneous catalysis a tailored contribution of shape selectivity and activity can lead to high-precision chemical conversion. However, up to now there have been very few data concerning the adsorption properties of light hydrocarbons in the all-silica DD3R.

This chapter presents adsorption data of ethane, ethene, propane, propene, and unsaturated linear C$_4$ molecules in the all-silica DD3R measured by the inertial microbalance technique, TEOM. An interpretation of the difference in the adsorption behavior for all the adsorptives investigated is given, based on their critical-molecular diameters. The conventional and dual-site Langmuir isotherm models have been used to describe the adsorption data. Furthermore, thermodynamic properties, like isosteric heat and entropy of adsorption, are presented to characterize interactions between adsorptive and adsorbent.

6.2 Experimental

A Rupprecht & Patashnick TEOM 1500 mass analyzer was used in an experimental set-up designed for measurement of equilibrium and transient adsorption on microporous materials. A detailed description of the TEOM apparatus is given in chapter 1 of this thesis.

Samples of 48.7 mg and 44.2 mg of the all-silica DD3R crystals were used for the adsorption experiments of C$_2$ and C$_3$ hydrocarbons and of unsaturated linear C$_4$ adsorptives, respectively. Quartz wool was used at the top and the bottom of the sample bed to keep the adsorbent particles firmly packed, which is essential for a stable measurement. The isotherms were obtained by a step-wise increase of the partial pressure of the feed gas at fixed
temperatures. The partial pressure of the feed gas was determined by its fraction of the total molar-feed-flow rate through the sample bed and the total pressure. A mixture of helium and the sample gas was used to create partial pressures below \(1.013 \times 10^5\) Pa and pure adsorptive gas was used for pressures above \(1.013 \times 10^5\) Pa.

The isotherm data were measured in different pressure ranges with a range of 0-1 \(\times 10^5\) Pa and 1-5 \(\times 10^5\) Pa for C\(_2\) and C\(_3\) hydrocarbons and of 0-1.5 \(\times 10^5\) Pa for unsaturated linear C\(_4\) adsorptives. It is necessary because of the importance of the data in the low-pressure region for accurate determination of the Henry’s law constant. The temperature range covered was from 303 to 473 K. Six temperatures were used for each adsorptive to reduce the uncertainty in the derived thermodynamic properties. Most experiments were duplicated, and both adsorption and desorption experiments were performed to confirm reversibility.

Prior to the experiments the crystals were outgassed in the following way. After a temperature rise with a rate of 10 K min\(^{-1}\) in \textit{ situ} in a helium flow rate of 200 cm\(^3\) (NTP) min\(^{-1}\) (NTP: room temperature and 1.013 \(\times 10^5\) Pa), the sample was heated at 573 K for 24 hours in order to remove adsorbed impurities.

Helium was obtained as an ultra-high purity gas (>99.999%). The gaseous adsorptives ethane, ethene, propane, and propene were 3.5 grade (>99.95%). The unsaturated linear C\(_4\) adsorptives but-1-ene, \textit{cis}-but-2-ene, \textit{trans}-but-2-ene, and buta-1,3-diene were obtained from Messer Griesheim, with specified purities over 99%, and were used without further purification.

The all-silica DD3R crystals had been synthesized in-house.\(^8\) The template inside the clathrasil DD3R crystals was removed by calcination at 973 K for 6 hours. The apparent density of the all-silica DD3R was 1.714 g cm\(^{-3}\) and the adsorption of N\(_2\) indicated an accessible microporous void volume of 0.15 cm\(^3\) g\(^{-1}\). The crystal size is in the range of 5-10 \(\mu m\), as determined by SEM, shown in Figure 6-2.

### 6.3 Theoretical Considerations

#### 6.3.1 Molecular dimensions and adsorbent pore systems
Knowledge of the dimensions of adsorptive molecules is crucial to understanding molecular exclusions as well as shape and size selectivity in microporous materials. Collision diameters or Lennard-Jones potential constants, \(\sigma\)\(_K\), have been employed to determine the accessibility of molecules to channels and/or apertures in microporous materials. The collision diameter is the intermolecular distance of closest approach for two molecules colliding as the potential is equal to zero.\(^9\) By assuming that the molecule is effectively spherical, the minimum
equilibrium diameter of a molecule, \( r_{\text{min}} \), is given by a Lennard-Jones 12-6 potential, i.e.
\[
1 \quad r_{\text{min}} = 2^{\frac{\kappa}{6}} \sigma_K.
\]

Webster et al.\(^{10}\) pointed out that collision diameters do not take into account molecular orientation, and this orientation is crucial in determining whether a molecule will fit into a small pore of fixed size. In addition, for large, nonspherically symmetrical molecules, collision diameters can not be used directly in determining whether the molecule can enter a pore.

Table 6-1 Characteristic diameters of the adsorptive molecules studied

<table>
<thead>
<tr>
<th>Adsorptive</th>
<th>( \sigma_K ) (nm)(^a)</th>
<th>( \sigma_S ) (nm)(^b)</th>
<th>( \sigma_C ) (nm)(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethane</td>
<td>0.38</td>
<td>0.206</td>
<td>0.372</td>
</tr>
<tr>
<td>ethene</td>
<td>0.39</td>
<td>0.178</td>
<td>0.344</td>
</tr>
<tr>
<td>propane</td>
<td>0.43</td>
<td>0.280</td>
<td>0.446</td>
</tr>
<tr>
<td>propene</td>
<td>0.45</td>
<td>0.265</td>
<td>0.431</td>
</tr>
<tr>
<td>but-1-ene</td>
<td>0.45</td>
<td>0.280</td>
<td>0.446</td>
</tr>
<tr>
<td>cis-but-2-ene</td>
<td>0.328</td>
<td></td>
<td>0.494</td>
</tr>
<tr>
<td>trans-but-2-ene</td>
<td>0.265</td>
<td></td>
<td>0.431</td>
</tr>
<tr>
<td>buta-1,3-diene</td>
<td>0.265</td>
<td></td>
<td>0.431</td>
</tr>
</tbody>
</table>

\(^{a}\) Collision diameter.\(^9\) \(^{b}\) Structural diameter defined as the diameter of the smallest cylinder that can be drawn around the molecule in its most favorable conformation through the centers of the extreme binding atoms.\(^{11}\) \(^{c}\) Critical diameter calculated by the summation of the structural diameter and the effective Van der Waals radii of the two extreme hydrogen atoms.

A better criterion of molecular exclusion is to use the critical dimensions of adsorptive molecules, based on the molecular structure and effective Van der Waals radii of extreme atoms. The structural diameter, \( \sigma_S \), which can be calculated from bond lengths and angles, is defined as the diameter of the smallest cylinder that can be drawn around the molecule, in its most favorable conformation, through the centers of the extreme binding atoms.\(^{11}\) For the hydrocarbons investigated, the effective Van der Waals radii of the two extreme hydrogen atoms must be taken into account. The Van der Waals radius of hydrogen is about 0.12 nm.\(^{12}\) By subtracting its atomic radius, 0.037 nm,\(^{13}\) the net contribution to the critical diameter is about 0.166 nm. Table 6-1 shows the three characteristic diameters of the hydrocarbon molecules studied. In contrast to the transient diameter, the alkene molecule has a smaller critical diameter than that of the corresponding alkane with the same carbon number. The cross-section of a methyl group is approximately circular while that a methylene group is more elliptical. In addition, a double bond can decrease the curvature of the molecule. Therefore, it is reasonable to expect that the alkene molecule has a smaller critical diameter, compared to that of the corresponding alkane.
6.3.2 Adsorption isotherms

Based on the critical diameters of the hydrocarbons studied, one may assume that the adsorption only takes place inside the 19-hedron cavities, entering via eight-membered rings of the all-silica DD3R. For the regular structure it is instructive to express the adsorptive location in terms of molecules per unit cell. The number of adsorbed molecules per unit cell, \( q \), is given by

\[
q = \frac{m_{\text{ads}}}{m} \frac{M_{\text{ac}}}{M_{\text{mol}}}
\]  

(6-1)

where \( M_{\text{ac}} \) and \( M_{\text{mol}} \) are respectively the molar weight of the unit cell and the molar weight of the adsorptive, and \( m_{\text{ads}} \) and \( m \) represent the adsorbed mass of the adsorptive and the mass of the adsorbent used, respectively. The number of molecules per unit cell is converted into that of molecules per cavity by dividing the number of cavities per unit cell, i.e. 6. This corresponds with a loading of 0.832 mol kg\(^{-1}\).

Adsorption isotherms provide a quantitative measure of the heterogeneous equilibria involved in the adsorption of a gas by a solid. A generalized description of heterogeneous equilibria uses the Langmuir equation that can be derived from transient, thermodynamic, or statistical mechanical considerations,\(^ {14-15} \) and which is often found to be satisfactory for zeolites due to compensation effects.\(^ {16} \) If the average number of molecules inside the 19-hedron cavity is \( \leq 1 \), interaction only takes place between adsorptive and adsorbent. Thus, the isotherms might be described by the conventional Langmuir model, eqn. (6-2),

\[
q = q_{1, \text{sat}} \frac{K_1 p}{1 + K_1 p}
\]

(6-2)

where \( q_{1, \text{sat}} \) is the saturation concentration of the molecules adsorbed per unit cell, \( K_1 \) is an equilibrium constant, \( p \) is the equilibrium pressure of the adsorptive, and the subscript 1 represents the adsorption process at loadings up to one molecule per cavity. This model implies that all adsorption sites are equivalent and that each site only contains a single molecule that does not interact with any neighboring molecule. When the number of molecules per cavity exceeds one, interaction between adsorptives will occur. This probably leads to deviations from the Langmuir model.

In view of the free volume, the 19-hedron cavity is capable to accommodate more than one molecule for light hydrocarbons. The adsorption of the second molecule will be energetically different. To describe this adsorption at higher loadings, a dual-site Langmuir (DSL) model is proposed. This model takes into account implicitly interactions between adsorptives, which give rise to a pseudo-second adsorption site.

\[
q = q_{1, \text{sat}} \frac{K_1 p}{1 + K_1 p} + q_{2, \text{sat}} \frac{K_2 p}{1 + K_2 p}
\]

(6-3)

with the subscript 2 referring to the adsorption at the second "site".
6.4 Results

6.4.1 Isotherms
The isotherm data of ethane, ethene, propene, trans-but-2-ene, and buta-1,3-diene adsorbed in the all-silica DD3R are presented in Figures 6-3 to 6-7. The isotherms were reversible over the complete pressure range investigated. For the sake of clarity, the desorption points are omitted. The isotherm data of propane in the all-silica DD3R are not presented, because the uptake was relatively slow and the equilibria were far from reached after 6 hours at a temperature between 303 and 473 K and pressures up to $5 \times 10^5$ Pa. The obtained loadings of propane were more than ten times smaller than those of propene. A transient uptake of propane and of propene is given in Figure 6-8, illustrating these observations.

For but-1-ene and cis-but-2-ene, the mass-uptake curves recorded with the TEOM are shown in Figure 6-9. Both mass uptakes take about 15 seconds to reach the steady state.

![Figure 6-3 Adsorption isotherms of ethane in the all-silica DD3R. Lines are the Langmuir isotherm model fits. (♦) 303 K; (▲) 338 K; (●) 373 K; (▼) 408 K; (●) 438 K; (■) 473 K.](image)

![Figure 6-4 Adsorption isotherms of ethene in the all-silica DD3R. Lines are the Langmuir isotherm model fits. (♦) 303 K; (▲) 338 K; (●) 373 K; (▼) 408 K; (●) 438 K; (■) 473 K.](image)
Figure 6-5 Adsorption isotherms of propene in the all-silica DD3R. Lines are the Langmuir isotherm (solid) and the dual-site Langmuir isotherm (dashed) model fits. (✦) 303 K; (▲) 338 K; (●) 373 K; (▼) 408 K; (◆) 438 K; (■) 473 K.

Figure 6-6 Adsorption isotherms of trans-but-2-ene in the all-silica DD3R. Lines are the Langmuir isotherm model fits. (✦) 303 K; (▲) 338 K; (●) 373 K; (▼) 408 K; (◆) 438 K; (■) 473 K.

Figure 6-9 also shows the reference run for but-1-ene. The apparent mass change for the reference run is caused by the change in the gas density. By subtracting this mass change, the amount adsorbed for 1-butene is 0.0155 mg in 44.2 mg of the all-silica DD3R, corresponding to 0.035 wt.%. For cis-but-2-ene, the amount adsorbed is in the same range as that of but-1-ene under the same conditions.

Compared to but-1-ene and cis-but-2-ene, the mass uptakes for trans-but-2-ene and buta-1,3-diene take much longer time to reach the equilibrium state, and the apparent mass changes are much higher. Figure 6-10 shows the mass-uptake curves of trans-but-2-ene and buta-1,3-diene at 373 K. Under these conditions, both mass changes caused by the changes in the gas density are in a range of 3 μg. The isotherm data of but-1-ene and cis-but-2-ene are not presented here, because the apparent mass uptakes were comparable to those of the relevant runs at a temperature between 303 and 473 K and pressures up to $1.5 \times 10^5$ Pa. So, essentially they do not adsorb.
Figure 6-7 Adsorption isotherms of buta-1,3-diene in the all-silica DD3R. Lines are the Langmuir isotherm model fits. (➕) 303 K; (△) 338 K; (●) 373 K; (▼) 408 K; (♦) 438 K; (■) 473 K.

Figure 6-8 Uncorrected mass uptakes of single components, propane and propene, and their mixture in the all-silica DD3R (48.7 mg) in flowing He [200 cm³ (NTP) min⁻¹] at 373 K and 1.013 × 10⁵ Pa (total). (a) Propane (2.5 × 10⁵ Pa); (b) propene (2.5 × 10⁴ Pa); (c) propane (2.5 × 10⁴ Pa) and propene (2.5 × 10⁴ Pa); (d) reference run of propane (2.5 × 10⁴ Pa).

The isotherms of ethane, ethene, propene, trans-but-2-ene, and buta-1,3-diene adsorbed in the all-silica DD3R exhibit a type-I adsorption isotherm, according to the Brunauer classification, over the temperature and pressure range studied, as shown in Figures 6-3 to 6-7. Both the Langmuir model and the DSL model, see eqns. (6-2) and (6-3), were used to fit the isotherm data, and indicated in Figures 6-3 to 6-7. The Langmuir model gives a good description of the isotherm data for ethane, ethene, trans-but-2-ene, and buta-1,3-diene. For the adsorption of propene at 303 and 338 K, deviations from the Langmuir model are observed at high loadings. The DSL model gives a significantly better description. If the DSL model is used to fit the results obtained at a high temperature, the parameters of one of the two terms become very small. The adsorption parameters obtained from the fits are listed in Table 6-2.
Table 6-2 Adsorption isotherm parameter values estimated for ethane, ethene, propene, trans-but-2-ene, and buta-1,3-diene

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<tr>
<th>Adsorptive</th>
<th>Adsorptive</th>
<th>( T )</th>
<th>( q_{sat,1} ) ( \text{m.u.c.}^b )</th>
<th>( q_{sat,2} ) ( \text{m.u.c.}^b )</th>
<th>( K_1 ) ( \times 10^{-5} \text{ Pa}^{-1} )</th>
<th>( K_2 ) ( \times 10^{-5} \text{ Pa}^{-1} )</th>
<th>( \sigma_{\text{model}}^a ) ( \text{m.u.c.}^b )</th>
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<td>K</td>
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<td></td>
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<td>2.47 ± 0.02</td>
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\(^a\) Standard deviation. \(^b\) 95% confidence error. \(^c\) Results for the dual-site Langmuir model.
Figure 6-9 Uncorrected mass uptakes of single components in the all-silica DD3R (44.2 mg) in flowing He [200 cm³ (NTP) min⁻¹] and a reference run at 338 K and 1.013 at 373 K and 1.013 × 10⁵ Pa (total). (a) Cis-but-2-ene (3 × 10⁴ Pa); (b) but-1-ene (2.8 × 10⁴ Pa); (c) reference run of but-1-ene (2.8 × 10⁴ Pa).

Figure 6-10 Uncorrected mass uptakes of single components, trans-but-2-ene and buta-1,3-diene in the all-silica DD3R (44.2 mg) in flowing He [200 cm³ (NTP) min⁻¹] at 338 K and 1.013 at 373 K and 1.013 × 10⁵ Pa (total). (a) Trans-but-2-ene (1.08 × 10⁴ Pa); (b) buta-1,3-diene (1.19 × 10⁴ Pa).

The various results, presented in Table 6-2 and Figures 6-3 to 6-7, show that the temperature and the molecular dimension have a pronounced effect on the adsorption of the light hydrocarbons in the all-silica DD3R. In the further analysis fitted model isotherms were used for the estimation of thermodynamic adsorption properties.

6.4.2 Thermodynamic properties

From the isotherm data a number of thermodynamic properties have been derived. The Henry’s law constant, \( K_H \), quantifies the extent of adsorption of a given adsorptive by a solid. The magnitude of \( K_H \) depends on both the properties of the adsorptive and solid. As a first estimation of the Henry’s law constant, its value can be obtained from the estimated parameter values in the conventional Langmuir model, \( K_H = K_1 q^\infty_1 \). An alternative way of representing the equilibrium data to extract the Henry’s law constant makes use of the virial form of the thermodynamic equilibrium relation.¹⁷
Figure 6-11 $\ln K_H$ vs $1/T$ plots for the studied adsorptives by the all-silica DD3R. (♦) Ethane; (▲) ethene; (●) propene; (▼) trans-but-2-ene; (❤) buta-1,3-diene.

$$p = \frac{q}{K_H} \exp\left(2B_1 q + \frac{3}{2}B_2 q^2 + \frac{4}{3}B_3 q^3 + \ldots\right)$$

(6-4)

where $K_H$ is the Henry’s law constant, $q$ the amount adsorbed, $p$ the equilibrium pressure, and $B_i$ the virial coefficient. It is evident that $\ln (p/q)$ versus $q$ should approach linearity at low loadings, thus providing a straightforward extrapolation to determine the Henry’s law constant $K_H$. The $K_H$ values obtained in this way, at the different temperatures, can be described with the integrated form of the Van’t Hoff equation,

$$K_H = K_{H0} \exp\left(\frac{-\Delta U^0}{RT}\right)$$

(6-5)

The observed linearity of the $\ln K_H$ vs $1/T$ plots, Figure 6-11, leads to the internal energy for adsorption at zero coverage, $\Delta U^0$, summarized in Table 6-3.

<table>
<thead>
<tr>
<th>Adsorptive</th>
<th>$K_{H0}$ $^{a}$</th>
<th>$-\Delta U^0$</th>
<th>$Q^a$</th>
<th>$\alpha$ $^{b}$</th>
<th>$d$ $^{c}$</th>
<th>$\nu_d \times 10^{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethane</td>
<td>$2.22 \times 10^{-9}$</td>
<td>24.7</td>
<td>24.8</td>
<td>4.43</td>
<td>0.321</td>
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<td>ethene</td>
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<td>26.7</td>
<td>24.3</td>
<td>4.25</td>
<td>0.251</td>
<td>2.46</td>
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<tr>
<td>propene</td>
<td>$1.58 \times 10^{-9}$</td>
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<td>36.0</td>
<td>6.26</td>
<td>0.454</td>
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<td>trans-but-2-ene</td>
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<td>41.1</td>
<td>8.49</td>
<td>0.697</td>
<td>2.09</td>
</tr>
<tr>
<td>buta-1,3-diene</td>
<td>$6.75 \times 10^{-10}$</td>
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<td>40.2</td>
<td>8.64</td>
<td>0.643</td>
<td>2.11</td>
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$^{a}$ Pre-exponential factor for the Van’t Hoff relation-equ. (6-5).  
$^{b}$ Polarizability.$^{29}$  
$^{c}$ Van der Waals constant, $a = 3 P_c V_c^2$, data from the critical point ($P_c$, $V_c$) from literature.$^{31}$  
$^{d}$ Approximate mean frequencies of molecules in the adsorbed state, calculated relative to Ar on KCl,$^{36}$ using $-\Delta U_l = 6.66$ kJ mol$^{-1}$, $m_1 = 39.91 \times 1.662 \times 10^{-24}$ g, and $\nu_1 = 1 \times 10^{12}$ s$^{-1}$ in eqn. (6-16).
Figure 6-12 Isosteric heat of adsorption as a function of the amount adsorbed. (∗) Ethane; (▲) ethene; (●) propene; (▼) trans-but-2-ene; (◆) buta-1,3-diene.

The isosteric heat of adsorption is defined by eqn. (6-6),\(^\text{18}\)

\[
\left[ \frac{\partial \ln p}{\partial T} \right]_q = \frac{Q^\infty}{RT^2}
\]  \hspace{1cm} (6-6)

So \(Q^\infty\) can be obtained from a plot of \(\ln p\) against the reciprocal of the temperature. Figure 6-12 shows the results of the isosteric heat of adsorption as a function of the amount adsorbed. Extrapolation then gives the isosteric heat of adsorption for the limiting case of adsorption at zero coverage, \(Q^\infty_0\), and presented in Table 6-3. The calculated isosteric heat of adsorption at zero coverage is independent of the temperature.

If \(Q^\infty\) and the differential adsorption enthalpy are assumed to be identical by neglecting any small temperature dependence, the differential molar entropy, \(\overline{S}_{\text{ads}}\), of adsorptive in the adsorbed phase can be calculated by eqn. (7).\(^\text{16}\)

\[
\overline{S}_{\text{ads}} = \overline{S}^0_v(298.15) + \int_{298.15}^T C_p \frac{dT}{T} + R \ln \left( \frac{P_0}{P} \right) - \frac{Q^\infty}{T}
\]  \hspace{1cm} (6-7)

where \(\overline{S}^0_v(298.15)\) is the standard molar entropy of the gas phase at \(T = 298.15\) K and \(P_0 = 1.013 \times 10^5\) Pa. \(C_p\) is the molar heat capacity of gaseous adsorptives at constant pressure and \(T\) and \(P\) are the equilibrium pressure and temperature. \(\overline{S}^0_v\) and \(C_p\) are obtained from literature.\(^\text{19}\) Values of \(\overline{S}_{\text{ads}}\) were determined at each of the experimental temperatures for ethane, ethene, propene, trans-but-2-ene, and buta-1,3-diene and were plotted as a function of the amount adsorbed. Results are illustrated for ethane, propene, trans-but-2-ene, and buta-1,3-diene in Figure 6-13. \(\overline{S}_{\text{ads}}\) increases with temperature and decreases with increasing loadings. The curves of \(\overline{S}_{\text{ads}}\) at different temperatures never intersect and follow parallel courses.
Figure 6-13 Differential entropy as a function of the amount adsorbed. Points correspond to the data calculated from eqn. (6-7). (○) 303 K; (△) 338 K; (●) 373 K; (▽) 408 K; (●) 438 K; (■) 473 K; (a) ethane; (b) propene; (c) trans-but-2-ene; (d) buta-1,3-diene.

6.5. Discussion

6.5.1 Shape selectivity
The critical diameters of both ethane and ethene are smaller than the free cross diameter of the eight-membered ring and their molecules easily enter the 19-hedron cavities. Under the same conditions, for the adsorption of ethane and ethene, there is no significant difference in the amount adsorbed in the all-silica DD3R.

It is interesting to note the difference in the adsorption behavior between propane and propene, as shown in Figure 6-8. The critical diameters of both propane and propene are comparable to the free cross diameter of the eight-ring window (see Table 6-1). For propane, the mass uptake recorded with the TEOM shows that the amount adsorbed is much lower than that of propene under the same conditions. Figure 6-8 also shows the mass uptake of binary mixture of propane and propene, which is the same as that of propene at the same partial pressure. This indicates that the presence of propane hardly affects the adsorption of propene. Apparently, the eight-ring windows exclude propane molecules. The small amount adsorbed is probably caused by adsorption on the external surface of the DD3R crystals.

The critical diameter of a propene molecule is slightly smaller than that of propane. The isotherm data show that the eight-ring windows of the 19-hedron cavities are accessible to propene molecules. At 303 K and a pressure over $4 \times 10^5$ Pa, a maximum amount adsorbed, about 8.9 molecules per unit cell, seen in Figure 6-5, was obtained. The uptake of propene, shown in Figure 6-8, indicates that its equilibrium adsorption takes a long time. Such a phenomenon can be interpreted in terms of the accessibility of the cavities through the eight-
ring window, since the critical diameter of propene molecule is close to the free-cross diameter of the eight-ring window. Also the orientation of the propene molecule to enter the eight-ring window and to move to the next cavity will play a role.

The different adsorption behaviors between propane and propene in the all-silica DD3R have been interpreted by means of simulations with the program Cerius². The simulation results indicate energy barriers of 30 and 90 kJ mol⁻¹ for propene and propane, respectively, as the molecules are forced through the rigid eight-membered ring window.²⁰ For a propane molecule, the angle between two C-C bonds will increase from about 113 to 125⁰, resulting in the internal deformation of the molecule, if the molecule is forced to pass through the window.

A similar shape-selective adsorption for the unsaturated linear C₄ molecules in the all-silica DD3R has been observed (see Figures 6-9 and 6-10). The critical diameters of both trans-but-2-ene and buta-1,3-diene are slightly smaller than the free cross diameter of the eight-membered ring and their molecules can enter into the 19-hedron cavities. However, the critical diameter of cis-but-2-ene is larger than the window size of the eight-membered ring and the critical diameter of but-1-ene is comparable to the eight-ring aperture. The results shown in Figures 6-9 and 6-10 indicate that the eight-ring windows are accessible to trans-but-2-ene and 1,3-butadiene molecules, while they exclude but-1-ene and cis-but-2-ene molecules. The small amount adsorbed for either but-1-ene or cis-but-2-ene is probably caused by adsorption on the external surface or defects of the DD3R crystals or to trace impurities from the gas phase adsorbed inside the 19-hedron cavities. In view of the fast attainment of these adsorption levels the adsorption at the external surface is the most probable explanation.

6.5.2 Isotherms
The isotherm data of both ethane and ethene are well described by the Langmuir model over the temperature and pressure range studied. Especially, for propene, deviations from the Langmuir model have been observed at 303 and 338 K and the higher-pressure range, at which the amount adsorbed exceeds 6 molecules per unit cell (see Figure 6-5). The molecular dimensions increase in order of ethene, ethane, and propene. The deviation from the Langmuir model also follows the same order. A plausible reason is that interactions between adsorptives result in the deviation from the Langmuir model as the number of molecules residing the 19-hedron cavity exceeds one. Obviously, increasing molecular dimensions can significantly enhance such an interaction.

The measured maximum amounts adsorbed at 303 K for both trans-but-2-ene and buta-1,3-diene are about six molecules per unit cell, corresponding to one molecule per the 19-hedron cavity. All estimated values for saturation amounts adsorbed at the temperatures investigated are in good agreement with this maximum loading. It is concluded that the maximum loading of either trans-but-2-ene or buta-1,3-diene in the all-silica DD3R is limited to one molecule per cavity. In agreement with this the isotherm data are well fitted by the Langmuir model, included in Figures 6-6 and 6-7.
Other isotherms including Dubinin, Temkin, Unilan and Tóth isotherms have been considered. From the fitted results, the Langmuir isotherm fits the present case best over all its range, except for propene at lower temperatures. For engineering purpose the Langmuir isotherm works very well and can be well applied.

6.5.3 Diffusion

For the simplest case involving only a single diffusional resistance inside the micropores, the uptake rate can be linked by a mass balance equation over an adsorbent crystal and its boundary conditions. The mass balance equation describing the temporal concentration distribution of the adsorbed species in a spherical crystal takes the following form

$$\frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D r^2 \frac{\partial q}{\partial r} \right)$$

(6-8)

where $D$ is the intracrystalline diffusivity and $r$ is the crystal-radius coordinate. The boundary conditions are

$$\frac{\partial q}{\partial r} \bigg|_{r=0} = 0; \quad q_{t=R} = q_{t=0} \frac{K_t P}{1 + K_t P}$$

(6-9)

![Figure 6-14 Uptake curve of propene at 373 K and 2.5 x 10^5 Pa (total pressure: 1.013 x 10^5 Pa). (a) Uptake data; (b) fitted by the diffusion model.](image)

Often well-defined large crystals with a uniform crystal size are used to determine intracrystalline diffusivities. Since the crystal size was not uniform in this study, the diffusional time constant $\bar{R}^2 / D$ ($\bar{R}$ is the average crystalline radius) is being fitted from the uptake curves. If one makes the simplifying assumptions that the concentration of adsorptive in the gas phase and the intracrystalline diffusivity are constant, the only unknown parameter, $\bar{R}^2 / D$, can be determined by nonlinear least squares estimation. The nonlinear least squares method consists of minimizing the sum of the squared difference between the data predicted by the model and the experimental data. Figure 6-14 represents a fitting example for propene uptake in DD3R at 373 K. The model fits the uptake data well. The fitted values of the characteristic diffusion time for propene, trans-but-2-ene, and buta-1,3-diene at 373 K are
also presented in Table 6-4. The diffusion of propene in DD3R is slightly faster than buta-1,3-diene and trans-but-2-ene.

Table 6-4 Diffusional time constants in DD3R at 373 K

<table>
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<tr>
<th>Adsorbive</th>
<th>propene</th>
<th>trans-but-2-ene</th>
<th>buta-1,3-diene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{R^2}{D}$ (s)</td>
<td>$7.2 \times 10^3$</td>
<td>$9.3 \times 10^3$</td>
<td>$1.0 \times 10^4$</td>
</tr>
</tbody>
</table>

6.5.4 Separations

Cryogenic distillation has been the dominant technology utilized for light alkane/alkene separations for many years. Although traditional distillation is reliable and essentially unchallenged in this application, the necessary low temperatures and high pressures make it an energy-intensive separation scheme because of the small difference in their relative volatility.\(^{21}\)

The use of molecular sieves and some Ag\(^+\)-substituted resins and CuCl/\(\gamma\)-Al\(_2\)O\(_3\) to perform propane/propane separations has been investigated by numerous researchers.\(^{22-25}\) Studies with 13X molecular sieves indicated that propane and propene can be separated using an equilibrium adsorption step followed by a variable-temperature stepwise desorption (VTSD).\(^{26}\) An economic comparison showed that the VTSD energy costs were lower, but capital costs were higher, than a comparable distillation process. Therefore, a process configuration based on a hybrid adsorption/distillation system has been considered to be an attractive commercial arrangement. This commercial process for light alkane/alkene separation is licensed by UOP Inc.\(^{27}\)

However, the regeneration cycles of commercial zeolites like those of 13X, 5A, and 4A are complicated and difficult. Due to catalytic action of these materials to alkene oligomerization at high temperatures, which can lead to coke formation and eventually block the adsorbents, the necessary vacuum swing adsorption processes at temperatures as low as 298 K are applied to the regeneration cycles.\(^{23}\) Furthermore, these hydrophilic zeolites are sensitive to water. Thus, these inherently difficult regeneration cycles and the addition of feed pretreatment steps negatively impact the process economics and may make this technology impractical.

The findings in this study eliminate these drawbacks of the separation processes based on the commercial zeolites. The all-silica DD3R is a highly hydrophobic and inert adsorbent, which is stable up to high temperatures. Although, the separations do not seem to be very economical due to the low uptake rates in the current adsorbent, it might be pointed out that the all-silica DD3R has potential applications in the challenging industrial separation processes. The rates of the uptakes can be enhanced by means of reducing the DD3R crystal size or increasing the operating temperature. Its potential application in separation is being further investigated.

The C\(_4\) fractions, obtained as by-products from petroleum refinery and petrochemical plants, usually first go through a butadiene extraction unit in which the butadiene is removed. Then but-2-enes can be separated from but-1-ene and isobutene by distillation.\(^{28}\) However, cis-but-2-ene and trans-but-2-ene cannot be economically separated into pure components by
conventional distillation because they are close boiling isomers (boiling points 276.86 and 274.03 K for cis-but-2-ene and trans-but-2-ene, respectively). The all-silica DD3R might be effective as a selective adsorbent for the separation or purification of but-2-ene mixtures.

6.5.5 Adsorption thermodynamics

For many applications of microporous materials, the equilibrium constants for the various processes are of prime concern. The Henry's law constants of either ethane and ethene or trans-but-2-ene and buta-1,3-diene in the all-silica DD3R are almost identical. At the same temperature, the value of the Henry's law constant increases with increasing the number of C-atom in the molecule, as shown in Figure 6-11. This indicates that a larger adsorptive molecule has a stronger affinity to the adsorbent.

The isosteric heat of adsorption for the adsorptives studied as a function of the amount adsorbed is presented in Figures 6-12. At loadings below one molecule per unit cell, the observed linearity of the $Q^a$ vs $q$ plots leads to the isosteric heat of adsorption at zero coverage, given in Table 6-3. The isosteric heat of adsorption at zero coverage increases in order of ethene, ethane, propene, buta-1,3-diene, and trans-but-2-ene. The all-silica DD3R is hydrophobic and stable to high temperatures. It provides a nonpolar structure for adsorption of relatively small gas molecules. For the nonspecific interactions involved, the adsorption potential is almost entirely the product of dispersion forces, where the adsorbent-adsorptive interaction is proportional to the polarizability of the adsorptive. The polarizability increases with increasing molecular dimensions, as shown in Table 6-3, which accounts for the fact that the isosteric heat of adsorption at zero coverage increases with increasing molecular dimensions. A similar reasoning can be followed for the Van der Waals constant, $a$, which is a measure of the attractive force between the molecules, also included in Table 6-3. This gives an explanation for the trend in the derived thermodynamic adsorption properties.

The derived $Q^a$ as a function of the amount adsorbed shows different trends at loadings below 6 molecules per unit cell for the $C_2$ and $C_3$ hydrocarbons. For ethane and ethene, $Q^a$ gradually increases with increasing loadings, which is the generally observed behavior for homogeneous adsorbents and non-specific interaction. On the other hand, for propene, $Q^a$ slightly decreases in a linear trend up to 6 molecules per unit cell, although the change in the isosteric heat of adsorption at low loadings is small. Similar observations have been made for the adsorption of $H_2O$ in the all-silica DD3R. Both molecules have a permanent dipole, so it is suggested that this behavior be due to specific interactions. But a clear interpretation cannot be given on the basis of the results. In view of the wide range of loadings over which this trend is present, a surface heterogeneity is not a probable explanation. The results in Figure 6-12 indicate that the DD3R shows reasonable energetic homogeneity, at least towards the small adsorptive molecules.

The $Q^a$ tends to sharply rise with increasing adsorption at loadings above 6 molecules per unit cell, shown in Figure 6-12, which is not only ascribed to molecule-molecule interactions within the 19-hedron cavities of DD3R but also due to the more confined packing, up to 1.5 molecules per cavity.
For the longer chain-length molecules *trans*-but-2-ene and buta-1,3-diene, at higher loadings, some significant changes in the isosteric heat as a function of the amount adsorbed can be seen in Figure 6-12. A plausible reason is that interactions between adsorbives develop at the higher fraction of sites covered. This leads to an increase in the isosteric heat of adsorption.

The differential molar entropy in the adsorbed phase, \( \overline{S}_{\text{ads}} \), gradually decreases with increasing loadings, and the same trend for all five adsorbives as a function of the amount adsorbed has been observed, as illustrated in Figure 6-13. The sigmoid form of the curves is expected for type-I isotherms. Barrer\textsuperscript{33} pointed out that the adsorption entropy is a characteristic function of the amount adsorbed. For energetically uniform adsorbents, \( \overline{S}_{\text{ads}} \) decreases continuously as \( q \) increases, while for energetically heterogeneous adsorbents, \( \overline{S}_{\text{ads}} \) often increases as \( q \) increases. So, also these data suggest that the all-silica DD3R can be considered as an energetically uniform adsorbent.

If the adsorbed molecules are oscillators, then \( \overline{S}_{\text{ads}} \) can be written as the sum of a configurational part, \( \overline{S}_c \), and a thermal part, \( \overline{S}_t \):\textsuperscript{16}

\[
\overline{S}_{\text{ads}} = \overline{S}_c + \overline{S}_t \quad (6-10)
\]

The \( \overline{S}_c \) gives the differential entropy of the three vibrational degrees of freedom, associated with the movement of the molecule about its mean position over the adsorption site. The differential configurational entropy, \( \overline{S}_c \), arises from the number of distinguishable configurations of adsorptive molecules on adsorption sites. For the Langmuir isotherm, eqn. (6-2), \( \overline{S}_c \) is given by eqn. (6-11).

---

Figure 6-15 Differential thermal entropy of adsorption as a function of the amount adsorbed. (✦) 303 K; (▲) 338 K; (●) 373 K; (▼) 408 K; (◆) 438 K; (■) 473 K; (a) ethane; (b) propene; (c) *trans*-but-2-ene; (d) buta-1,3-diene.
\[ S_c = -R \ln \left( \frac{\Theta}{1 - \Theta} \right) \]  

where \( \Theta \) corresponds to the fraction of sites covered. Equations (6-10) and (6-11) were used to evaluate \( S_a \), as a function of the amount adsorbed, shown in Figure 6-15. At lower loadings, \( S_a \) is approximately independent of \( q \), again indicating homogeneous adsorption, approaching Langmuir assumptions. For the \( C_2 \) and \( C_3 \) adsorbives, at higher loadings, a pronounced decrease of \( S_a \) is seen. Here, more than one molecule is forced into the 19-hedron cavities. Therefore, the molecules will lose more degrees of freedom. For larger dimension molecules \( \text{trans-but-2-ene} \) and \( \text{buta-1,3-diene} \), interactions between adsorbives residing in neighboring 19-hedron cavities develop at higher loadings, resulting in a pronounced decrease in the freedom of the adsorbed molecules.

From eqn. (6-11) it follows that at \( \Theta = 0.5 \) for Langmuir adsorption \( S_c \) is equal to zero, implying that \( S_a \) and \( S_{ads} \) are identical. This is also defined as the standard state of adsorption for the Langmuir model. For polyatomic hydrocarbon molecules, the thermal entropy of the adsorbed phase can be expressed as the sum of three terms,\(^{16, 34}\)

\[ S_a = \bar{S}_V + \bar{S}_I + \bar{S}_R \]  

(6-12)

where \( \bar{S}_V \) is the differential vibrational entropy of the adsorbed molecule as a whole; \( \bar{S}_I \), the differential entropy associated with the internal vibrational and rotational degrees of freedom; and \( \bar{S}_R \), the differential rotational entropy of the adsorbed molecule as a whole.

Following the procedure described by Barrer\(^{34}\) and Eberly\(^{35}\), \( \bar{S}_V \) can be estimated by the following equation

\[ \bar{S}_V = 3 \left( \bar{S}_V = 3R \left( \frac{h\nu}{kT} \frac{\exp (h\nu/kT) - 1}{1 - \exp (-h\nu/kT)} \right) - \ln \left( 1 - \exp (-h\nu/kT) \right) \right) \]  

(6-13)

The quantity \( \nu \) is the vibrational frequency of the hydrocarbon molecule as a whole in its intracrystalline environment. The estimation of this vibrational frequency follows the procedure previously described by Barrer\(^{34}\). For argon adsorbed on potassium chloride, Ott\(^{36}\) calculated the potential energy-distance curve for an argon atom situated over the center of a KCl lattice cell. By plotting the region round the minimum on a large scale, the value of the restoring force per unit displacement, \( f \), was obtained by fitting the potential energy-distance curve using eqn. (6-14),

\[ -\Phi = \frac{1}{2} f (r - r_e)^2 \]  

(6-14)

where \( \Phi \) is the total potential energy, \( r \) the distance of the atom in any position above the surface, and \( r_e \) the equilibrium distance. Since

\[ \nu = \frac{1}{2\pi} \sqrt{\frac{f}{m}} \]  

(6-15)

where \( m \) is the reduced mass of the oscillator, and as a reasonable assumption the restoring force is proportional to the energy of adsorption, then \( \nu \) will be directly proportional to the
square root of the energy of adsorption.\textsuperscript{16, 37} Equation (6-16) was used to derive approximate mean frequencies for hydrocarbons in the all-silica DD3R.

\[
\frac{v_1}{v_2} = \sqrt{\frac{f_1 m_2}{f_2 m_1}} = \sqrt{\frac{\Delta U/m_2}{\Delta U/m_1}} \tag{6-16}
\]

where $\Delta U$ is the energy of adsorption. The calculated mean frequencies are included in Table 6-3.

Table 6-5 Entropy values in J mol\textsuperscript{-1} K\textsuperscript{-1} for the adsorption of ethane, ethene, propene, \textit{trans}-but-2-ene, and buta-1,3-diene in the all-silica DD3R at $\theta = 0.5$

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<th>Adsorptive</th>
<th>$T$ (K)</th>
<th>$\bar{S}_V$ \textsuperscript{a}</th>
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<th>$\bar{S}_a$</th>
<th>$\bar{S}_V$ \textsuperscript{b}</th>
<th>$\Delta S(3V)$ \textsuperscript{c}</th>
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\textsuperscript{a} Calculated from eqn. (6-13). \textsuperscript{b} Calculated from eqn. (6-18).

\textsuperscript{c} $\Delta S(3V) = \bar{S}_V [\text{eqn. (6-18)}] - \bar{S}_V [\text{eqn. (6-13)}]$. 

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The sum of $S_s(g) + S_r(g)$ in the gas phase can be obtained by subtracting the three-dimensional translational entropy, $S_{\text{std}}(g)$, from the standard entropy of the gaseous hydrocarbon.

$$S_{\text{std}}(g) = R \ln \left( M^{1.5} T^{2.5} \right) - 9.61 \tag{6-17}$$

where $M$ is the molar weight (g mol$^{-1}$) and $T$ is the temperature (K). By assuming that the internal vibrational and rotational entropy remains unaltered upon adsorption, the differential vibrational entropy of the adsorbed molecule, $\overline{S}_V$, can be estimated by eqn. (6-18),

$$\overline{S}_V = \overline{S}_a - \left[ S^0(g) - S_{\text{std}}(g) \right] \tag{6-18}$$

where $S^0(g)$ is the standard molar entropy in the gaseous phase at the standard pressure of 1.013 x $10^5$ Pa. So, there are two ways to estimate $\overline{S}_V$, from an average vibrational frequency, eqn. (6-13), and from the differential thermal entropy, eqn. (6-18). Summary calculations of the entropy of ethane, ethene, propene, trans-but-2-ene, and buta-1,3-diene in the adsorbed phase at $\theta = 0.5$ are included in Table 6-5. As can be seen, there is a considerable discrepancy between the differential vibrational entropy calculated by eqn. (6-13) and that by eqn. (6-18). This difference changes little over the temperature range studied. This difference is interpreted as that the adsorbed molecules still possess some translational mobility inside the 19-hedron cavities. Eberly$^{35}$ gave a similar interpretation on the adsorption of cyclohexane in Na mordenite.

### 6.6 Conclusions

The adsorption isotherms of ethane, ethene, propene, trans-but-2-ene, and buta-1,3-diene in the all-silica DD3R have been accurately measured using the TEOM technique over a wide pressure and temperature range relevant to practical applications. At loadings below 6 molecules per unit cell, the Langmuir model gives a good description of the amount adsorbed inside the 19-hedron cavities, which can be considered as energetically uniform sites for adsorption. The saturated amount adsorbed corresponds to one molecule per 19-hedron cavity for trans-but-2-ene and buta-1,3-diene. For propene below 340 K a dual-site Langmuir model better represents the adsorption data. Thermodynamic properties like isosteric heat and entropy of adsorption have been determined, which are in agreement with the physical picture of the localized adsorption on a homogeneous adsorbent.

Only minor differences exist between the adsorption of ethane and ethene. Propene molecules are strongly adsorbed in the cages of the all-silica DD3R, while propane does not become adsorbed. The result of the mass uptake of their mixture implies that the fact that the two gases are mixed is irrelevant to the degree of separation possible. In addition, a high selectivity for trans-but-2-ene over cis-but-2-ene in this material has been observed. The all-silica DD3R, which is inert, hydrophobic, and stable up to high temperatures and has a good capacity for the adsorption of propene and trans-but-2-ene, might be effective as a selective adsorbent for the separation of either propane and propene mixtures or but-2-ene mixtures.
Acknowledgment

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References

Summary and Evaluation

7.1 Introduction

Adsorption and diffusion of adsorptive and/or reactant in microporous materials are most important phenomena occurring in a variety of processes of great practical relevance such as separation and purification by adsorption, heterogeneous catalysis, etc. In spite of continuous theoretical and experimental efforts dedicated to its study for many years, adsorption in microporous materials still presents many unsolved problems associated with energetic heterogeneity affecting adsorption at the gas/solid interface in a variety of ways. Adsorption experiments have shown more and more discrepancies between theory and experiment. As the theoretical adsorption isotherms could not be successfully used to fit experimental data, various empirical equations have been used for that purpose. The theory of micropore filling, developed by Dubinin and co-workers, is a major contribution to adsorption science, alongside the Langmuir and BET isotherms. This approach was based on Polanyi’s idea of adsorption potential, which was assumed to be different in different micropores. An implicit assumption was made that the adsorption proceeds in a stepwise fashion in micropores in the sequence of decreasing adsorption potential. The idea of the Dubinin-Radushkevich (DR) equation is related to the geometric heterogeneity of porous solids. However, deviations between the DR equation and the experimentally observed behavior of microporous adsorption systems have been reported more and more frequently. The modification of the DR equation does not solve the raised problem as well.

Zeolites are crystalline materials, and presumably each unit cell is equivalent to the other. Many zeolites of industrial interest possess a pore structure consisting of three-dimensional arranged cavities. These cavities are usually connected by windows having a smaller size.
More than one molecule can usually be accommodated in each cavity. Due to the restricted size of the window that connects neighboring cavities, the interaction of molecules adsorbed in neighboring cavities is largely screened. For MFI-type zeolites, there are two intersecting channel systems, a straight channel and a zigzag channel, forming a three-dimensional pore network. Therefore, the concept of energetic heterogeneity in zeolites is limited to the number of type of 'sites'. Different models can describe the adsorption in different types of pore structures. Moreover, zeolites are the perfect candidates to apply statistical thermodynamic analyses. In recent years, adsorption science in zeolites has been developed along molecular simulations, which take account of more detailed mechanicistic models inside micropores.1

The measurement of micropore diffusion in zeolite crystals and other microporous solids has proven a far more challenging task than might have been anticipated. The developments of microscopic techniques such as the pulsed-field-gradient nuclear-magnetic resonance (PFG-NMR) and quasi-elastic neutron scattering (QENS) methods for measuring self-diffusion under equilibrium conditions have proven to be a major milestone. For many experimental systems, diffusivities yielded by the PFG-NMR and QENS measurements are several orders of magnitude larger than the values derived from traditional macroscopic measurements. Most of the more obvious explanations of these remarkable discrepancies between determined diffusivities by the microscopic and macroscopic techniques have been considered and shown to be inapplicable.2 The application of the microscopic methods is expected to have a significant progress on the study of adsorption kinetics. However, such an application has been limited by the short relaxation times of many adsorbed molecules. Inherently, the macroscopic techniques are still being developed and widely used for measuring diffusivities in microporous materials. The in-house adsorption/diffusion research with the Multitrack technique has demonstrated that the determined adsorption and diffusion constants are in agreement with those from the microscopic methods.3

Yet, recent improvements in instrumentation have made available "push-button" systems for simultaneously measuring adsorption isotherms and kinetics. The design of experimental techniques has been carried out towards to the low uncertainties of final results.

A novel microbalance technique-the tapered element oscillating microbalance (TEOM), as applied to measurements of adsorption and diffusion properties of microporous materials, has been applied and evaluated throughout this thesis. The combined effects of energetic heterogeneity and interactions between adsorbed molecules on the adsorption behavior have been observed and the understanding of such effects, from a theoretical point of view, has been approached. An example has been given for determining the diffusivities of linear and branched C₆ alkanes in silicalite-1 by the TEOM technique. A detailed model has been proposed for that.

In this chapter, the main conclusions obtained in this study are summarized. An evaluation is given of the potential separations of linear and branched alkanes by silicalite-1 adsorbents or membranes and of propane/propane mixtures by the all-silica-DD3R as well as of the potential applications of the TEOM technique to study adsorption and diffusion in microporous materials.
7.2 Summary

7.2.1 Adsorption in silicalite-1
The isotherm data of normal C$_1$ to C$_4$ alkanes and $n$-hexane in silicalite-1, determined by the TEOM technique, are in good agreement with the literature data measured by other techniques so far. This agreement indicates that the TEOM is a reliable technique. The isotherms of single-branched alkanes such as isobutane, 2-methylpentane, and 3-methylpentane, for the first time, experimentally show a two-step adsorption behavior in silicalite-1.

Silicalite-1 can be considered as a good model adsorbent for testing adsorption isotherm models, based on gas-solid molecular interactions. The reconciliation of the experimental data and molecular simulations provides an excellent interpretation of the adsorption in terms of a volume filling processes with two different spaces for light-normal alkanes and single-branched alkanes in silicalite-1 structure. This can be described by a dual-site Langmuir (abbreviated as DSL) expression. The single-branched alkanes prefer to reside in the channel intersections, while the normal alkanes indeed prefer to sit in the channels. These preferential locations inside silicalite-1 are caused by energetic heterogeneity between the channels and the intersections. The derived thermodynamic properties such as adsorption enthalpy and entropy from the DSL model are in good agreement with those available from other techniques in literature. The observed two-step adsorption behavior for the single-branched alkanes in silicalite-1 is attributed to the large difference in the adsorption entropy between the molecular locations in the intersections and in the channels. The credibility of the proposed approach is enhanced by its ability to provide meaningful thermodynamic properties.

A small “kink” in the isotherm for $n$-hexane at four molecules per unit cell of silicalite-1 has been observed; this is in agreement with results from other techniques. To fill the entire silicalite-1 structure neatly, the $n$-hexane molecules located in the zigzag channels have to be “frozen” in these channels. This “freezing” of the positions of the $n$-hexane molecules means a regular ordering and implies a loss of entropy and therefore will occur only if the pressure (or gas-phase chemical potential) is sufficiently high to compensate for this loss. Therefore, this configurational-entropic effects lead to adsorption heterogeneity. At loadings below four molecules per unit cell, $n$-hexane molecules can sit in either the straight or the zigzag channels with the intersections. Globally, at those conditions a homogeneous adsorption site can be considered. However, at loadings over four molecules per unit cell, the adsorption of the adsorbing molecules “frozen” in the zigzag channels will be energetically different. This gives rise to a pseudo-second-adsorption site. The DSL model implicitly reflects the adsorption behavior of $n$-hexane in silicalite-1 with two different energetic configurations.
7.2.2 Diffusion in silicalite-1
The diffusion of linear and branched C<sub>6</sub> alkanes in silicalite-1 has been investigated using the TEOM technique. Model equations, in which the thermodynamic factor for intracrystalline diffusivities has been taken into account, enable the determination of the diffusivities from adsorption and desorption patterns operated in the non-linear range and bypass simplifying assumptions for analytic solutions. The determined diffusivities at zero coverage for the studied adsorptives are in good agreement with those available measured by the ZLC method.

Unlike the conventional gravimetric method, the TEOM technique minimizes external mass and heat transfer limitations in transient experiments due to a high flow rate of the carrier gas through the sample bed without affecting measurements. The chromatography and/or ZLC techniques, which are widely used to determine micropore diffusivities currently, seem to be suitable for measuring the gas uptake or the desorption pattern due to a continuous-flow system. Often the operation is performed in the linear adsorption range and the diffusivities or diffusion time constants can be fitted by simple analytic equations under certain assumptions for the initial or for the long time data. The latter approach is usually followed; this yields the linear relationship of the logarithm of concentration in a dimensionless form as a function of time. The operation in the linear adsorption range also indicates that the ZLC method is applicable only for weakly adsorbing systems. In addition, in the ZLC technique the composition of the gas mixture must be accurately determined from the desorption stream. The determination becomes critical for low concentrations at long desorption times, and just those data are used for the analysis. The TEOM technique measures the integral sample-mass change with a good time resolution and stability. It can be easily used not only for steady state and equilibrium measurements, but also for transient uptake and desorption experiments. Moreover, the proposed models were able to investigate the concentration-dependent diffusivities.

7.2.3 Adsorption in the all-silica DD3R
The adsorption isotherms of ethane, ethene, propene, <i>trans</i>-but-2-ene, and buta-1,3-diene in the all-silica DD3R have been reported for the first time over a wide pressure and temperature range relevant to practical applications. At loadings below 6 molecules per unit cell, the conventional Langmuir model gives a good description of the amount adsorbed inside the 19-hedron cavities, which can be considered as energetically uniform sites for adsorption. The saturated amount adsorbed corresponds to one molecule per 19-hedron cavity for <i>trans</i>-but-2-ene and buta-1,3-diene. For propene below 340 K a dual-site Langmuir model better represents the adsorption data. Only minor differences exist between the adsorption of ethane and ethene. Thermodynamic properties like isosteric heat and entropy of adsorption have been determined, which are in agreement with the physical picture of the localized adsorption on a homogeneous adsorbent. In addition, the characteristic diffusion times are estimated from the uptake curves for propene, <i>trans</i>-but-2-ene, and buta-1,3-diene. The diffusion of propene in the all-silica DD3R is slightly faster than <i>trans</i>-but-2-ene and buta-1,3-diene.

Propene molecules are strongly adsorbed in the cages of the all-silica DD3R, while propane does not become adsorbed. The result of the mass uptake of their mixture implies that
the fact that the two gases are mixed is irrelevant to the degree of separation possible. In addition, high selectivity for trans-but-2-ene over cis-but-2-ene in this material has been observed. The all-silica DD3R, which is inert, hydrophobic, and stable up to high temperatures and has a good capacity for the adsorption of propene and trans-but-2-ene, might be effective as a selective adsorbent for the separation of either propane and propene mixtures or but-2-ene mixtures.

7.3 Evaluation

7.3.1 Separations of linear and branched alkanes by silicalite-1
The loss of the adsorption entropy for single-branched alkane molecules residing in the channels is more than that for corresponding normal alkanes. This also indicates that normal alkanes have a higher packing efficiency than the branched ones within the silicalite-1 structure. Examples have been shown for n-butane/isobutane in chapter 3 and for n-hexane/2-methylpentane and/or 3-methylpentane in chapter 4. Thus these entropic effects might be applied to the separation of linear and branched alkane isomers by silicalite-1 adsorbents or membranes. The initial filling of the channels by normal alkane molecules and the intersections by branched alkane molecules will consequently not be independent processes due to the spatial phenomena, and non-ideal behavior is expected. The mixture isomers of n-hexane and 2-methylpentane, determined by the CBMC simulations, show a curious maximum in the loading of 2-methylpentane; this loading decreases to almost zero with increasing pressure due to the entropic effects that the adsorbed 2-methylpentane molecules can be squeezed out by n-hexane at higher pressures, since a packing efficiency is much higher for n-hexane within the silicalite-1 structure. This leads to a high adsorption selectivity for n-hexane. Unfortunately, the experimental mixture isotherm data are rarely available, because binary measurements are experimentally at least an order of magnitude more complicated and time consuming, compared to single component measurements. In principle, binary isotherms can be determined using the TEOM technique. These experimentally determined binary isotherm data would be very useful to confirm the prediction by the CBMC simulations and to support the concept that molecular packing efficiencies and preferential adsorption can separate branched and straight-chain alkanes by silicalite-1.

7.3.2 Separations by the all-silica DD3R
The close boiling points of propane and propene mean that cryogenic distillation, while costly in energy terms, has been used in the industry for some 20 years, because an alternative method has simply not been found until now. A process configuration based on a hybrid adsorption/distillation system has been considered to be an attractive commercial arrangement. For that purpose, it is of utmost importance to find an effective adsorbent. The all-silica DD3R is a highly hydrophobic and inert material, which is stable up to high temperatures. High selectivity for propene over propane has been found in this study. But the separation does not seem to be very economical by the current adsorbent due to a long
characteristic diffusion time ($\frac{\bar{R}^2}{D}$), which is in the order of $10^4$ s at 373 K. However, the characteristic diffusion time can be dramatically reduced with decreasing the crystal size. So, the potential application to the economical separation of propane-propene mixtures might be possible if the smaller crystals of the all-silica DD3R can be synthesized.

Another potential application of the DD3R might be the kinetic separation of smaller molecules, for instance, ethane-ethene mixtures. A slight difference in the molecular-critical diameter will lead to a significant difference in the kinetic behavior in the DD3R.

7.3.3 Applications of the TEOM technique
The TEOM technique has been used to investigate catalytic kinetics and catalyst deactivation in the form of coking. This technique has been also applied to measurements of adsorption and diffusion of single components in microporous materials.

Applications of microporous adsorbents become increasingly important in industry. Yet, binary gas adsorption, even the simplest case, cannot be reliably predicted from pure component information. The determination of mixture isotherms is demanded but mostly limited by adsorption techniques. Therefore there have been hardly mixture isotherms available so far. The use of the TEOM might enable the measurement of binary isotherm data, for instance, hexane isomers in silicalite-1. If desorption is a relatively slow process, in principle, the concentrations in the outlet of the TEOM unit could be analyzed on-line. This enables the determination of binary adsorption data.

In the numerical approach presented in chapter 5 of this thesis, the simplifying assumptions about gas phase concentrations and constant diffusivity were not required, but the proper relations were used. Therefore, the concentration dependency of diffusivities could be incorporated. This is easily extended to analyze data from simple variants of the stimulus response technique applied in the TEOM to study self-diffusion and counter-diffusion in binary systems.

References

Appendix A

Thermodynamic Factor of a Dual-Site Langmuir Model

A dual-site Langmuir model has the following generalized form.

\[ q = q_A^{\text{sat}} \frac{K_A p}{1 + K_A p} + q_B^{\text{sat}} \frac{K_B p}{1 + K_B p} \quad (A-1) \]

where the parameter or variable has the same significance as that in the text. To derive the thermodynamic factor the pressure is expressed in the loading \( q \), as follows

\[ p = \frac{C_1}{2 K_A K_B \left\{ q_A^{\text{sat}} + q_B^{\text{sat}} \right\} - q} \quad (A-2) \]

with

\[ C_1 = \left( q_A^{\text{sat}} K_A + q_B^{\text{sat}} K_B \right) - q \left( K_A + K_B \right) + \sqrt{C_2^2 + 4 q_A^{\text{sat}} K_A q_B^{\text{sat}} K_B} \quad (A-3) \]

in which

\[ C_2 = \left( q_A^{\text{sat}} K_A - q_B^{\text{sat}} K_B \right) - q \left( K_A - K_B \right) \quad (A-4) \]

The thermodynamic factor can be expressed:

\[ \Gamma = \frac{\partial \ln p}{\partial \ln q} = \frac{q}{p} \frac{\partial p}{\partial q} = q \left( \frac{C_3 + \frac{1}{q_A^{\text{sat}} + q_B^{\text{sat}} - q}}{C_1} \right) \quad (A-5) \]

with

\[ C_3 = \left( K_A + K_B \right) - \frac{\left( K_A - K_B \right) C_2}{\sqrt{C_2^2 + 4 q_A^{\text{sat}} K_A q_B^{\text{sat}} K_B}} \quad (A-6) \]

Then

\[ \frac{\partial \Gamma}{\partial r} = \left[ \frac{C_1 + C_4 q + q_A^{\text{sat}} + q_B^{\text{sat}}}{C_1} \left( \frac{q_A^{\text{sat}} + q_B^{\text{sat}} - q}{C_1} \right)^2 - \left( \frac{C_3}{C_1} \right) \right] \frac{\partial q}{\partial r} \quad (A-7) \]

with

\[ C_4 = \frac{4 q_A^{\text{sat}} K_A q_B^{\text{sat}} K_B \left( K_A - K_B \right)^2}{\left( C_2^2 + 4 q_A^{\text{sat}} K_A q_B^{\text{sat}} K_B \right)^{3/2}} \quad (A-8) \]
Appendix B

Plug Flow Model

The flow of a gas through a packed bed can generally be represented by the axial-dispersed plug-flow model. If the system is isothermal with negligible pressure drop and if the concentration of adsorptive in the gas phase is small, the gas velocity may be considered as constant through the sample bed and, under these conditions, the basic continuity equation, derived from a mass balance on an element of the void bed is

\[
\frac{\partial p}{\partial t} = -u \frac{\partial p}{\partial z} + D_L \frac{\partial^2 p}{\partial z^2} + \left( \frac{1-\epsilon}{\epsilon} \right) \left( a' D_0 R_k T \right) \left( \frac{\partial q}{\partial r} \right) \bigg|_{r=R_p}
\] (A-9)

where \(u\) is the gas velocity, \(z\) the spatial coordinate, and \(D_L\) the axial dispersion coefficient.

The boundary conditions in eqn. (A-9) are

\[
p|_{z=0} = p_n - \frac{D_L}{u} \frac{\partial p}{\partial z}; \quad z = L, \quad \frac{\partial p}{\partial z}|_{z=L} = 0
\] (A-10)

where \(L\) is the sample bed length. By assuming cylindrical particles, the solid phase mass balance is expressed in eqn. (5-3) in chapter 5. For a step change in adsorptive partial pressure from zero to \(p_0\) (adsorption) or from \(p_0\) to zero (desorption) at time \(t = 0\), the following dimensionless variables and parameters are defined:

\[
X = \frac{r}{R_p}; \quad Y = \frac{p}{p_0}; \quad Z = \frac{z}{L}; \quad Q = \frac{q}{q_0}
\] (A-11)

The mass balance eqn. (A-9) becomes

\[
\frac{\partial Y}{\partial t} = -\frac{u}{L} \frac{\partial Y}{\partial Z} + \frac{D_L}{L^2} \frac{\partial^2 Y}{\partial Z^2} + \left( \frac{1-\epsilon}{\epsilon} \right) \left( \frac{q_0}{p_0} \right) \left( a' D_0 R_k T \right) \left( \frac{\partial Q}{\partial X} \right) \bigg|_{X=L}
\] (A-12)

The mass balance over a cylindrical crystal in a dimensionless form is the same as eqn. (5-13) in chapter 5. The boundary conditions for a step change in the gas phase:

\[
Y|_{Z=0} = 1 - \frac{D_L}{uL} \frac{\partial Y}{\partial Z}; \quad \frac{\partial Y}{\partial Z}|_{Z=L} = 0 \quad \text{for adsorption}
\] (A-13)

\[
Y|_{Z=0} = -\frac{D_L}{uL} \frac{\partial Y}{\partial Z}; \quad \frac{\partial Y}{\partial Z}|_{Z=L} = 0 \quad \text{for desorption}
\] (A-14)

For a gaseous system the axial dispersion coefficient becomes independent of velocity only in the very low Reynolds number region. More generally the velocity dependence is given by an expression of the form\(^1\)

\[
D_L = 0.7 D_{AB} + \frac{u d_p}{2(1 + 10 D_{AB} / u d_p)}
\] (A-15)

where \(d_p\) is the particle diameter and \(D_{AB}\) the molecular diffusion coefficient of gas A in gas B.

The molecular diffusion coefficients for binary mixtures of nonpolar gases A and B can be predicted by kinetic theory.\(^2\)
\[ D_{AB} = \frac{1.8345 \times 10^{-7}}{p\sigma_{AB}^2\Omega_{D,AB}} \sqrt{T^3 \left( \frac{1}{M_A} + \frac{1}{M_B} \right)} \]  
(A-16)

in which \( D_{AB} \) [\( \text{m}^2 \text{s}^{-1} \)], \( T \) [\( \text{K} \)], \( p \) [\( \text{KPa} \)], \( \sigma_{AB} \) [\( \text{nm} \) units], \( M_A \) and \( M_B \) (molecular weight) [\( \text{g mol}^{-1} \)] and \( \Omega_{D,AB} \) is a dimensionless function of the temperature and of the intermolecular potential field for one molecule of A and one of B. The parameters \( \sigma_{AB} \) and \( \Omega_{D,AB} \) can be obtained with the potential field by the Lennard-Jones function:

\[ \varphi_{AB}(r_{AB}) = 4\varepsilon_{AB} \left( \frac{\sigma_{AB}}{r_{AB}} \right)^{12} - \left( \frac{\sigma_{AB}}{r_{AB}} \right)^{6} \]  
(A-17)

\( \Omega_{D,AB} \) for this potential energy model as a function of \( kT/\varepsilon_{AB} \) (\( k \): Boltzmann constant) can be found in literature.\(^2\)

The Lennard-Jones parameters \( \sigma_{AB} \) and \( \varepsilon_{AB} \) could, in principle, be made for nonpolar, nonreacting molecule pairs by combining ones of species A and B empirically:

\[ \sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B) \quad \text{and} \quad \varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B} \]  
(A-18)

When values of \( \sigma \) and \( \varepsilon \) are not known, they may be estimated from the properties of the fluid at the critical point by means of the following empirical relations\(^2\)

\[ \frac{\varepsilon}{k} = 0.77 T_c \quad \text{and} \quad \sigma = 0.52 \left( \frac{T_c}{p_c} \right)^{\frac{1}{2}} \]  
(A-19)

where \( T_c \) [\( \text{K} \)] and \( p_c \) [\( \text{kPa} \) units].

<table>
<thead>
<tr>
<th>( M_B ) (g mol(^{-1}))</th>
<th>( T_c ) (K)</th>
<th>( p_c ) (MPa)</th>
<th>( \sigma ) (nm)</th>
<th>( \varepsilon/k ) (K)</th>
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Table A-1 Critical point and Lennard-Jones parameters of He (B) from literature\(^2\)

<table>
<thead>
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<th>( A )</th>
<th>( M_A ) (g mol(^{-1}))</th>
<th>( T_c ) (K)(^a)</th>
<th>( p_c ) (MPa)(^a)</th>
<th>( \sigma ) (nm)(^b)</th>
<th>( \varepsilon/k ) (K)(^b)</th>
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<td>( n )-hexane</td>
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<td>507.5</td>
<td>3.018</td>
<td>0.628</td>
<td>390.8</td>
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<td>2-methylpentane</td>
<td>86.17</td>
<td>497.7</td>
<td>3.040</td>
<td>0.622</td>
<td>383.2</td>
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<td>3-methylpentane</td>
<td>86.17</td>
<td>504.6</td>
<td>3.120</td>
<td>0.620</td>
<td>388.5</td>
</tr>
<tr>
<td>2,3-dimethylbutane</td>
<td>86.17</td>
<td>500.0</td>
<td>3.150</td>
<td>0.616</td>
<td>385.0</td>
</tr>
</tbody>
</table>

\(^a\) Data from literature.\(^1\) \(^b\) Values calculated from eqn. (A-19).

<table>
<thead>
<tr>
<th>( A )</th>
<th>( \sigma_{AB} ) (nm)</th>
<th>( \varepsilon_{AB}/k ) (K)</th>
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<tr>
<td>( n )-hexane</td>
<td>0.443</td>
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<td>2-methylpentane</td>
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<td>3-methylpentane</td>
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<td>2,3-dimethylbutane</td>
<td>0.437</td>
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Table A-3 Derived Lennard-Jones parameters of alkane (A) and He (B) by eqn. (A-18).
Table A-4 Calculated values of $D_{AB}$ by eqn. (A-16) at a total pressure of 101.3 kPa and different temperatures

<table>
<thead>
<tr>
<th>A</th>
<th>$T$ (K)</th>
<th>$kT/\varepsilon_{AB}$</th>
<th>$\Omega_{D,AB}$</th>
<th>$D_{AB} \times 10^5$ (m$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-hexane</td>
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<td>338</td>
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<td></td>
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</tr>
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<td>388</td>
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<td></td>
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<td>408</td>
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<tr>
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<td>473</td>
<td>7.55</td>
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</table>

Figure A-1 $\Omega_{D,AB}$ as a function of $kT/\varepsilon_{AB}$. *: Data from literature. The line is fitted by the equation

$$\Omega_{D,AB} = 0.747 + 0.621 \exp\left(-0.377 \frac{kT}{\varepsilon_{AB}}\right).$$
Figure A-2 Uptake rate of 2,3-dimethylbutane with a partial pressure of 2.42 kPa, corresponding to $q_0 = 0.44$ molecules per unit cell, in silicalite-1 (20.4 mg) in flowing He with a rate of 100 cm$^3$ (NTP) min$^{-1}$ (NTP: room temperature and 101.3 kPa) at 473 K. The line is the model fit and (○) experimental data.

Figure A-2 shows an example for the uptake of 2,3-dimethylbutane in silicalite-1 fitted by eqns. (A-12) and (5-13). The estimated value of $D_0$ is $(1.46 \pm 0.03) \times 10^{-13}$ m$^2$ s$^{-1}$, which is very close to the data shown in Table 5-1, estimated from the CSTR model. Due to the thin layer of the silicalite-1 crystals used, with a mass between 10 and 20 mg, corresponding with 0.75 to 1.5 mm bed length, the concentration gradient in the sample bed is negligible. Both CSTR and plug flow models do not result in different estimated $D_0$ values. The result shown in Figure A-2 supports this consideration.
Appendix C

Influence of Geometry Choice on Estimated Diffusivities

A generalized mass-balance equation over a crystal can be expressed

\[ \frac{\partial q}{\partial t} = \frac{1}{r^s} \frac{\partial}{\partial r} \left[ D(q) r^s \frac{\partial q}{\partial r} \right] \]  
(A-20)

where \( s \) is the particle shape factor (\( s = 0, 1, \) and \( 2 \) for slab, cylinder, and sphere, respectively). The characteristic diffusion length \( R_p \) is defined

\[ R_p = (1 + s) \frac{V_p}{S_p} \]  
(A-21)

where \( V_p \) and \( S_p \) are the volume and external surface area of particle, respectively.

Figure A-3 shows a comparison of the models (CSTR) with a slab shape and with a spherical shape. For the sake of clarity, the fitting line for the model over a cylindrical crystal is not shown in Figure A-3. Both the cylindrical model and the spherical model fit the desorption curve well, whereas the model for a slab crystal does not describe the desorption curve properly. A comparison of the results fitted by the models with these three different crystal shapes is summarized in Table A-5. The cylindrical model fits the data best; the SSR value of the spherical model is always 30-50\% larger. The slab model is incapable of a proper description.

![Graph](image)

Figure A-3 Geometry effect on the fits (solid line: sphere and dashed line: slab) of the desorption curve for 2,3-dimethylbutane with a partial pressure of 2.40 kPa, corresponding to \( q_0 = 0.76 \) m.u.c., in silicalite-1 (20.4 mg) in flowing He with a rate of 100 cm\(^3\) (NTP) min\(^{-1}\) at 453 K.
Figure A-4 Comparison of the plots of ln \(D_0\) as a function of \(1/T\) for 2,3-dimethylbutane in silicalite-1. (▲) Model with a spherical shape; (▼) model with a cylindrical shape.

The estimated \(D_0\) value for a spherical shape is also consistently slightly larger than for a cylindrical one. Thus the values of the derived diffusional activation energy are also different. Figure A-4 shows this comparison for 2,3-dimethylbutane in silicalite-1. The diffusional activation energy for a spherical shape (58.0 kJ mol\(^{-1}\)) is about 5 kJ mol\(^{-1}\) lower than for a cylindrical shape. This also exemplifies a reason for discrepancies in diffusivity and diffusional activation energy values in literature due to a different geometry choice. The crystals used in this study have a cylindrical-like shape. It appeared that this consistently yielded the best description of the desorption profiles. Therefore, the presented diffusivities were determined for a cylindrical shape.

Table A-5 Comparison of the results fitted by the models with three different crystal shapes. The experimental conditions are shown in Figure A-3

<table>
<thead>
<tr>
<th>Geometry</th>
<th>(D_0 \times 10^{14}) (m(^2) s(^{-1}))</th>
<th>SSR(^a)</th>
<th>(\sigma_{\text{model}}) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cylinder</td>
<td>7.84 ± 0.01(^c)</td>
<td>3.30 \times 10^{-2}</td>
<td>9.49 \times 10^{-5}</td>
</tr>
<tr>
<td>slab</td>
<td>5.34 ± 0.03</td>
<td>1.85 \times 10^{-1}</td>
<td>5.34 \times 10^{-4}</td>
</tr>
<tr>
<td>sphere</td>
<td>9.49 ± 0.02</td>
<td>4.68 \times 10^{-2}</td>
<td>1.34 \times 10^{-4}</td>
</tr>
</tbody>
</table>

\(^a\) Defined by eqn. (5-16), \(^b\) Standard deviation, \(^c\) 95\% confidence error.

References


Samenvatting

Adsorptie en Diffusie in Microporeuze Materialen: Een Experimentele Studie met de TEOM

Adsorptie in Silicaliet-1

De adsorptie-isothermen van lineaire $C_1$ tot $C_4$ alkanen en hexaan in silicaliet-1 zijn bepaald met de TEOM techniek. Silicaliet-1 is een zeoliet met een hoge silica/alumina verhouding. In dit microporeuze materiaal kunnen drie adsorptieplaatsen worden onderscheiden: het rechte kanaal, het zigzagkanaal en de kruisingen tussen rechte en zigzagkanalen.

De betrouwbaarheid van de TEOM wordt geïllustreerd door de goede overeenstemming van de isothermen met de literatuurwaarden die tot nu gemeten zijn met andere technieken. Voor het eerst is een twee-staps adsorptie gedrag gevonden voor de isothermen van enkelvertakte alkanen, zoals isobutaan, 2-methyl-pentaan en 3-methyl-pentaan, in silicaliet-1.


Een kleine "knik" in de isotherm van hexaan bij vier moleculen per eenheidsecel is in overeenstemming met resultaten afkomstig van andere technieken. Om de hele structuur van
Samenvatting

Silicaliet-1 netjes op te vullen, moeten de hexaanmoleculen in de zigzagkanalen “bevriezen”. Deze regelmatige ordening houdt in dat hexaanmoleculen entropie moeten verliezen, wat alleen gebeurt als de druk (of de chemische potentiaal van de gasfase) voldoende hoog is om het entropieverlies te compenseren. Het entropische effect van de verschillende configuraties leidt dus tot een heterogeniteit in de adsorptie. Bij beladingen beneden vier moleculen per eenheidsec kunnen hexaanmoleculen zich bevinden in zowel de rechte kanalen als in de zigzagkanalen met de kruisingen. De adsorptieplaatsen kunnen bij deze condities dus als homogezen worden beschouwd. Bij meer als vier moleculen per eenheidsec zal de adsorptie van de “bevroren” moleculen in de zigzagkanalen energetisch gaan afwijken. Er wordt bij deze hogere beladingen dus een tweede adsorptieplaats waargenomen (de zogenaamde pseudo-tweede adsorptieplaats). Het DSL model zal dit gedrag van hexaan in silicaliet-1 met twee verschillende energetische configuraties dan ook goed beschrijven.

Diffusie in Silicaliet-1

De diffusie van lineaire en vertakte C₅ alkanen in silicaliet-1 is ook met de TEOM techniek onderzocht. Voor de verwerking van de transiënte data zijn modelvergelijkingen opgesteld, waarin de thermodynamische factor voor interkristallijne diffusie is opgenomen. Dit maakt de bepaling van de diffusiesnelheden bij hogere beladingen mogelijk. De diffusiesnelheden bij een bedekking van nul (diffusiviteiten at zero coverage), die bepaald zijn voor verschillende gassen, zijn in overeenstemming met de ZLC (zero-length column) methode.

In tegenstelling tot de conventionele gravimetrische methode minimaliseert de TEOM techniek externe stof- en warmte-transportbeperkingen in transiënte experimenten zonder de metingen te verstoren. Dit komt door een hoog debiet van draaggas door het monsterbed. De chromatografische en/of ZLC technieken, die tegenwoordig veel worden gebruikt om diffusiesnelheden in microporiën te bepalen, lijken geschikt te zijn voor het meten van de gasopname of het desorptiepatroon, omdat ze gebruik maken van een systeem met een continue stroom. Vaak worden deze metingen uitgevoerd in het lineaire adsorptiegebied. Hierdoor kunnen de diffusiesnelheden of diffusietijsconstanten worden gefit met eenvoudige, analytisch oplosbare vergelijkingen. Hiervoor zijn wel aannames nodig voor de initiële condities of voor de meetwaarden op lange termijn. De laatste aanpak wordt meestal gevolgd; dit levert een lineaire vergelijking op van de logaritme van de concentratie (in een dimensieloze vorm) als functie van de tijd. Operatie in het lineaire adsorptiegebied betekent echter dat de ZLC methode alleen toepasbaar is op systemen met een zwakke adsorptie. Bovendien moet voor de ZLC methode de samenstelling van het uitgaande gasmengsel nauwkeurig worden bepaald. Deze bepaling wordt moeilijk voor lage concentraties bij lange desorptietijden en juist deze data worden gebruikt voor de analyse. Met de TEOM techniek kan de geïntegreerde massaovergang met een goede tijdsresolutie en stabilititeit worden bepaald. De TEOM kan eenvoudig worden gebruikt voor zowel experimenten bij constante gasdebieten en evenwichten, maar ook voor experimenten met transiënte opname en desorptie. Bovendien stellen de voorgestelde modellen ons in staat concentratie-afhankelijke diffusiesnelheden te bestuderen.
Adsorptie in Silica DD3R


Propeenmoleculen adsorberen sterk in de holtes van silica DD3R, terwijl propaan helemaal niet adsorbeert. Gebleken is dat de scheidingsefficiency van propaan en propeen niet afhankelijk is van de propaan-propeen verhouding in het gasmengsel. Bovendien heeft trans-2-buteen een hoge selectiviteit ten opzichte van cis-2-buteen. Silica DD3R is inert, hydrofoob en stabiel tot hoge temperatuur en heeft een goede adsorptiecapaciteit voor propeen en trans-2-buteen. Industriële toepassing van silica DD3R in de scheiding van propaan/propeen of 2-buteen mengsels lijkt dus mogelijk te zijn.
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Weidong
Delft, The Netherlands
February 2001
List of Publications in 1998-2001


**Oral presentations**


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Curriculum Vitae

The author of this dissertation was born on June 8, 1963 in Zhejiang, China where he grew up and completed his M.Sc. degree in Physical Chemistry at the Department of Chemistry, Zhejiang University. In 1994 he started to study Chemical Engineering at the Delft University of Technology, The Netherlands, from which he graduated for M.Sc. (scheikundig ingenieur in Dutch) in February 1997. His M.Sc. thesis, entitled “The Effects of NOx and CO on the Rates of Transition Metal Oxides Catalyzed Soot Oxidation”, was carried out in the section of Industrial Catalysis, DelftChemTech, Faculty of Applied Sciences. In July 1997 he started working on his Ph.D. project with thesis advisors Prof. dr. Jacob A. Moulijn and Prof. dr. Freek Kapteijn in the same section. His research interests were in adsorption and diffusion in microporous materials, Fischer-Tropsch synthesis, and catalyst deactivation in the form of coking. The main results are included in this dissertation.

Since February 2001 he has been appointed as a post-doctoral fellow in the section of Industrial Catalysis, DelftChemTech, Faculty of Applied Sciences, Delft University of Technology. His current interest is in membrane separations.