Available online at www.sciencedirect.com

Journal of Catalysis 218 (2003) 135–147

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Pore mouth physisorption of alkanes on ZSM-22: estimation of physisorption enthalpies and entropies by additivity method

C.S. Laxmi Narasimhan,[a] J.W. Thybaut,[a] G.B. Marin,[a,*] J.A. Martens,[b] J.F. Denayer,[c]
and G.V. Baron[c]

[a] *Laboratorium voor Petrochemische Techniek, Universiteit Ghent, Krijgslaan 281, B-9000 Ghent, Belgium*
[b] *Centrum voor Oppervlaktechemie en Katalyse, Katholieke Universiteit Leuven, Kasteelpark Arenberg 23, B-3001 Heverlee, Belgium*
[c] *Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussel, Belgium*

Received 31 October 2002; revised 14 February 2003; accepted 17 February 2003

Abstract

ZSM-22 (TON-type) zeolite has a pore size close to that of alkanes and exhibits pronounced molecular sieve effects with alkanes. *n*-Alkanes physisorb through the pore mouths into the micropores while the iso-alkanes physisorb at the pore mouths only. Physisorption inside the micropores results in additional entropy and enthalpy loss compared to physisorption at the pore mouths. Multiple modes of physisorption exist at the pore mouths: each of the "straight ends" of the iso-alkane can protrude into the micropore. A two-step physisorption model distinguishing between physisorption at the pore mouths and subsequent transfer from pore mouths into the micropores has been developed. The standard physisorption enthalpy and entropy for each of the physisorption modes of iso-alkanes and *n*-alkanes are computed following an additivity principle. The Henry coefficient for each alkane is the sum of contributions calculated for the individual physisorption modes. The standard physisorption enthalpy and entropy for each alkane are calculated from the distribution of physisorption modes using ideal mixing rules.

Keywords: Hydrocracking; Hydroisomerisation; ZSM-22 zeolite; Molecular sieve; Shape selectivity; Alkanes; Pore mouth catalysis; Physisorption

1. Introduction

Molecular sieve-type zeolites are widely employed in many petroleum and petrochemical processes as they exhibit shape selectivity. ZSM-22 (TON-type), belonging to the group of 10-membered ring zeolites, is commercially applied for skeletal isomerisation of alkanes [1,2]. Due to its narrow channel structure (0.44 × 0.55 nm) [3] and resultant strong overlapping force fields exerted by the zeolite walls, ZSM-22 shows strong and peculiar physisorption characteristics. Changes in physisorption behaviour of reaction products compared to feed molecules have been used to explain shape-selective effects observed in processes such as hydrocracking and hydroisomerisation. Two different theories are found in the literature concerning this matter.

The first theory considers steric hindrance for physisorption of iso-alkanes inside the micropores due to their bulky size [4–19]. Henry coefficients are high for normal alkanes, while for iso-alkanes the Henry coefficients are significantly lower [4–6]. The saturation capacity for *n*-alkanes is 3 orders of magnitude higher than that for iso-alkanes. From the systematic observation of lower adsorption enthalpy and entropy of iso-alkanes compared to *n*-alkanes, it was concluded that, under reaction conditions, iso-alkanes do not access the micropores in contrast to *n*-alkanes [4–6].

Ocakoglu et al. [18] compared the physisorption properties of iso-alkanes on ZSM-22 samples with open pores and with blocked pores, respectively. They observed comparable standard physisorption enthalpies and entropies for iso-alkanes on both forms, suggesting that iso-alkanes do not penetrate and adsorb into "open" pores of ZSM-22. Significant differences between the physisorption properties of normal- and iso-alkanes were observed in open ZSM-22. Pronounced changes in physisorption properties for *n*-alkanes as compared to iso-alkanes were also found by Pieterse et al. [2] and lead to the conclusion that branched molecules can physisorb at the pore mouths of ZSM-22 only.

---

[*] Corresponding author.
E-mail address: guy.marin@rug.ac.be (G.B. Marin).

0021-9517/03/$ – see front matter © 2003 Elsevier Inc. All rights reserved.
doi:10.1016/S0021-9517(03)00069-1

These authors also postulated the existence of strong Brönsted acid sites at the pore mouth and the occurrence of subsequent acid-catalysed reactions at the pore mouth rather than on the external surface or inside the micropores of the zeolite crystallite. In the pore mouth mechanism, branched molecules physisorb in such a way that one of its “straight ends” protrudes into the pore mouth. Straight ends of an alkane are the unbranched terminal ends of the main alkyl chain and of the alkyl substituents of the latter. The carbon atom on which the straight end is attached is outside the pore. For longer molecules, which can span more than one pore mouth, key-lock configurations also exist, involving two or more pore mouths [12,15,16].

The second theory proposed by Maesen et al. [20,21] and Schenk et al. [22] favours product shape selectivity, based on differences in product diffusivities, along with transition state shape selectivity. Branched molecules are assumed to enter the micropore, and due to differences in diffusivities among the different product molecules, shape selectivity occurs. This theory was based on configurational bias Monte Carlo (CBMC) calculations for estimating intermolecular interactions and physisorption properties of n-alkanes and iso-alkanes inside the micropores of ZSM-22. It follows from the calculations that branched alkanes can enter the pores if properly oriented. The above theory seems to be in contradiction with classical bifunctional mechanism [23], which requires a very short time scale for diffusion of reactants from acid sites to metal sites, while inside ZSM-22 micropores large diffusion resistances exist due to a single-file diffusion mechanism [24]. Also, there are significant deviations between calculated physisorption properties using the CBMC technique and experimentally measured values [20].

In the pore mouth mechanism, different orientations of the iso-alkane molecules can exist, depending upon the straight end that has entered the pore mouth cavity. Due to varying force fields inside and outside the pore mouth cavity, each of these orientations, termed as “modes,” exhibits different physisorption properties. Each mode is characterised by the carbon atoms inside and outside of the pore mouth cavity. Chemisorption and subsequent acid-catalysed reactions occur at the pore mouth. As physisorption precedes protonating chemisorption, each individual physisorption mode determines the subsequent reactions and reaction intermediates. To model the corresponding reaction kinetics, the distribution of physisorbed alkanes among their possible physisorption modes as well as the changes in physisorption properties during the course of reaction have to be accounted for quantitatively. A typical reaction mixture for hydrocarbon conversion such as alkane hydroconversion is a multicomponent system involving alkanes and iso-alkanes in the reaction mixture. The pure component physisorption properties and Langmuir isotherms are used to describe the physisorption of the multicomponent reaction mixture either by classical Langmuir-based approaches or through ideal and real adsorption solution theories (IAST, RAST) [25–28].

The present paper aims at a model to describe the single-component physisorption phenomenon on ZSM-22 along with a methodology to calculate physisorption properties for n-alkanes and iso-alkanes for each of their individual pore mouth physisorption modes. The methodology is analogous to additivity methodologies for thermodynamic properties determination. Based on the estimates obtained for the additivity parameters, the physisorption properties are calculated and compared with experimental data [4–6,18]. The physisorption properties and the model to describe the multiple physisorption modes of pure components can be directly used in any of the above-mentioned methods to describe physisorption of the multicomponent reaction mixture.

2. Procedures and data

2.1. Sorbent

Data obtained before on two types of ZSM-22, an “open” and a “closed” form, have been used in the present work. The synthesis of the open form has been described in detail by Ernst et al. [29], while the closed form was obtained with the same procedure, however, without removal of the 1,6-diaminohexane template from the micropores. The silicon–aluminum ratio of ZSM-22 is 30 and the crystals have a needle-like shape with a length varying from 1 to 2 µm. The form of ZSM-22 synthesised following the normal recipe, i.e., with removal of the template and, hence, with free accessible pores, is referred to as open ZSM-22. The concentrations of pore mouths and Brönsted acid sites for the sorbent are listed in Table 1. An as-synthesised ZSM-22 zeolite sample with the template left inside the micropores is referred to as closed ZSM-22. Details about the latter can be found in Ocakoglu et al. [18].

2.2. Physisorption properties

The physisorption isotherm for alkane “i” based on Henry’s law is expressed as:

$$C_i = H_i p_i, \tag{2.1}$$

where C_i is the physisorbed alkane concentration. The Henry coefficient H_i is obtained from the expression

$$H_i = \left(\frac{C_{\mathrm{t},i}}{2p^\circ}\right) \mathrm{e}^{\Delta S^\circ_{\mathrm{phys},i}/R} \mathrm{e}^{-\Delta H^\circ_{\mathrm{phys},i}/(RT)}, \tag{2.2}$$

Table 1
Range of experimental conditions on ZSM-22 along with their critical characteristics [4–6,18]

	ZSM-22
Sorptive	C5–C9 (normal, mono-, di- and tri-branched)
Temperature (K)	473–623
$C_{\mathrm{t,pm}}$ (10^{-3} mol kg^{-1})	0.33
Total Brönsted acid sites ($\approx C_{\mathrm{t,mp}}$) (mol kg^{-1})	0.54

where $C_{t,i}$ is the total concentration of physisorption sites for alkane i and p° is the standard state pressure. The above expression is based on a standard state at which half of the active sites are occupied because of configurational entropy reasons [4–6,31]. The standard physisorption enthalpies and entropies are experimentally obtained from van't Hoff's plots.

2.3. Physisorption data

Denayer et al. [4–6,19], using a chromatographic method [30], have determined the low-coverage adsorption properties for normal and branched C5–C9 alkanes on open ZSM-22. The fact that adsorption of the studied alkanes was completely reversible and that no secondary peaks occurred during the measurements indicated that only physisorption occurred, and no chemical bounding or reaction took place [4,5,18]. Henry coefficients and standard physisorption enthalpies and entropies were reported. Ocakoglu et al. [18] have confirmed the findings of Denayer et al. [4–6,19].

For n-alkanes, the strong increase of the standard physisorption enthalpy loss with carbon number is accompanied by a high loss of rotational and translational freedom as the molecules are fully physisorbed inside the pores. For iso-alkanes, the physisorption enthalpies vary with the branching position and degree of branching. The standard physisorption enthalpy and entropy and, hence, Henry coefficients depend on the number of carbon atoms physisorbed inside the pores. Fig. 1 shows the values for the standard physisorption enthalpy on open and closed ZSM-22 as a function of carbon number for various classes of alkanes. A distinct linear relationship of the standard physisorption enthalpy and entropy with the carbon number is observed for each alkane class [4–6,19]

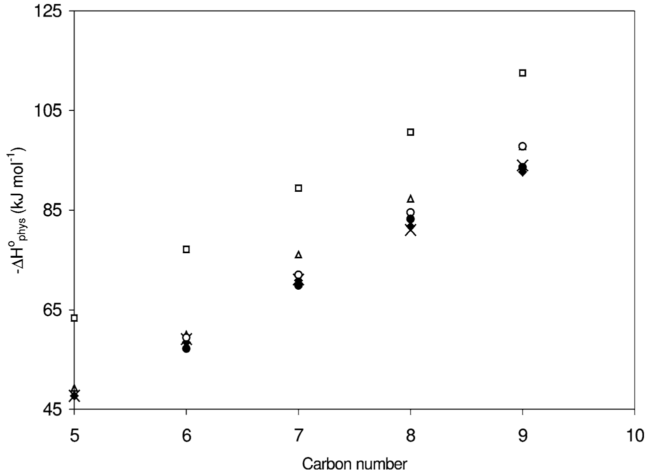


Fig. 1. Experimental standard physisorption enthalpy of C5–C9 alkanes and iso-alkanes on open [4–6] and closed [18] ZSM-22: (◆) n-alkanes in closed ZSM-22; (□) n-alkanes in open ZSM-22; (X) 2Me-branched alkanes in closed ZSM-22; (△) 2Me-branched alkanes in open ZSM-22; (●) 3Me-branched alkanes in closed ZSM-22; (○) 3Me-branched alkanes in open ZSM-22.

Table 2

Estimates with their 95% confidence intervals for the parameters of Eqs. (2.3) and (2.4) describing standard physisorption enthalpy and entropy for n-alkanes on open ZSM-22 [4–6] obtained through regression of Henry coefficient relationship with standard physisorption enthalpy and entropy, viz. Eq. (2.2) along with Eqs. (2.3) and (2.4) with the experimental Henry coefficient on open ZSM-22

Parameter	Open ZSM-22
α (kJ mol^{-1})	12.84 (±0.15)
β (kJ mol^{-1})	−2.3 (±0.8)
γ (J mol^{-1} K^{-1})	17.01 (±0.29)
δ (J mol^{-1} K^{-1})	28.84 (±0.19)

$$-\Delta H^\circ_{\mathrm{phys},i} = \alpha \mathrm{CN}_i + \beta, \tag{2.3}$$

$$-\Delta S^\circ_{\mathrm{phys},i} = \gamma \mathrm{CN}_i + \delta, \tag{2.4}$$

where CN_i represents the carbon number of the physisorbed alkane and α, β, γ, and δ are alkane class-dependent parameters. The carbon number dependence of the corresponding Henry coefficients follows from the substitution of Eqs. (2.3) and (2.4) into Eq. (2.2). Values for the open ZSM-22 parameters α, β, γ, and δ have been estimated by Denayer et al. [4] and Ocakoglu et al. [18] through regression of standard physisorption enthalpy and entropy obtained through van't Hoff's plots generated from experimental determination of Henry coefficients at different temperatures for each alkane class [4–6,18]. In the present work, Henry coefficients have been considered as responses for parameter estimation. Consistent with this, the parameters α, β, γ, and δ have been re-estimated considering Henry coefficients as responses. Estimation of parameters α, β, γ, and δ corresponding to the n-alkanes on open ZSM-22 viz., Table 2, are obtained from regression with Eq. (2.2) together with Eqs. (2.3) and (2.4) of the experimentally determined Henry coefficients of C5–C9 n-alkanes over the temperature range of 473–623 K [4–6,18] and extrapolated Henry coefficients for 623–673 K using van't Hoff's relationship as responses. The range of experimental conditions are given in Table 1. Ocakoglu et al. [18] have also determined the physisorption properties for n-alkanes and iso-alkanes on closed ZSM-22, viz., Fig. 1. Unlike open ZSM-22, closed ZSM-22, which has the template left inside the micropores, presents effectively only pore mouths and no micropores. For iso-alkanes it has been observed that physisorption enthalpies and entropies on closed ZSM-22 are comparable within 3–5 kJ mol^{-1} and 4–8 J mol^{-1} K^{-1}, respectively, to those obtained on open ZSM-22. For n-alkanes, the physisorption enthalpies and entropies are significantly less negative [18]. The corresponding values are close to those obtained for iso-alkanes on closed ZSM-22 as can be seen from Fig. 1. Physisorption of n-alkanes inside the micropores on open ZSM-22 is thermodynamically different from physisorption on closed ZSM-22, as it is accompanied by additional loss of entropy and enthalpy [18], which are practically carbon number-independent.

The standard physisorption enthalpy of monobranched alkanes on open ZSM-22 was observed to become less negative as the monobranching position moves toward the centre of the main alkyl chain of the alkane [5,18]. For example, standard physisorption enthalpy of 2-methylheptane is $-87.3\ \mathrm{kJ\,mol^{-1}}$ while that of 4-methylheptane is $-77.4\ \mathrm{kJ\,mol^{-1}}$. Moreover, the enthalpy loss upon physisorption of a branched alkane for which the longest straight end has i carbon atoms is higher than that of an n-alkane with i carbon atoms upon physisorption at the pore mouth:

$$-\Delta H^{\circ}_{\mathrm{phys(2MeC7)}} > -\Delta H^{\circ}_{\mathrm{phys}(n\mathrm{C6})} > -\Delta H^{\circ}_{\mathrm{phys}(n\mathrm{C5})}. \tag{2.5}$$

In its most stable physisorption mode, 2-methylheptane has five carbon atoms protruding inside the pore mouth. Assuming that carbon atoms outside the pore mouth exhibit no enthalpy loss, a standard pore mouth physisorption enthalpy for 2-methylheptane close to the standard micropore physisorption enthalpy for n-pentane is expected. However, the standard pore mouth physisorption enthalpy for 2-methylheptane is more negative than the standard micropore physisorption enthalpy for n-pentane and even than for n-hexane. Similar observations are made for other iso-alkanes.

The above observations indicate that standard physisorption enthalpy loss for iso-alkanes at pore mouths exists not only for carbon atoms protruding inside the pore mouths, but also for the carbon atoms outside the pore mouth. Denayer [6] and Martens et al. [9] have already postulated that, in the case of branched alkanes, apart from the interactions of carbon atoms inside the pore mouths, the carbon atoms outside also interact to a relatively lower extent with the external surface. Analogous observations can be made for standard entropy. The following trend of the Henry coefficients results:

$$H(\mathrm{2MeC7}) > H(\mathrm{nC6}) > H(\mathrm{nC5}). \tag{2.6}$$

All the iso-alkane molecules in the database, viz. Table 1, exhibit only a pore mouth configuration except 2-methylheptane, 2-methyloctane, and 3-methyloctane, which have additionally key-lock physisorption modes. These are the only molecules having a "straight end," which is long enough to traverse the bridge between two neighboring pore mouths and enter the second pore mouth with the tail of their long straight end while another, short straight end is in the first pore mouth. The requirement for the key-lock mechanism is that the length of the straight end has to be greater than the width of the bridge separating the pore mouths. This bridge width corresponds to at least three methylene groups of the straight end [12,15,16]. Because the description of pore mouth physisorption is the aim in the present paper, the alkanes exhibiting additional key-lock physisorption behaviour are not considered in the regression.

2.4. Parameter estimation

Estimation of the parameters is performed by minimisation of the weighted sum of squares of the residuals between the experimental and calculated Henry coefficients.

$$\mathrm{SSQ} = \sum_{j=1}^{\mathrm{nob}} w_j \left(H_j - H_j^{\mathrm{exp}}\right)^2, \tag{2.7}$$

H_j^{exp} is the experimental Henry coefficient corresponding to the jth observation, which pertains to an alkane at a given experimental temperature. Extrapolation based on van't Hoff's relation is carried out for obtaining H_j^{exp} for temperatures not covered by the experiments. As mentioned above, alkanes having only a pore mouth configuration are considered for parameter estimation. The total number of observations "nob" for parameter estimation for C5–C9 alkanes amounts to 50 for n-alkanes, 70 for monobranched alkanes, and 60 for multibranched alkanes. The weighting factor w_j is expressed as follows:

$$w_j = \frac{(H_j^{\mathrm{exp}})^{-1}}{\sum_j^{\mathrm{nob}} (H_j^{\mathrm{exp}})^{-1}}. \tag{2.8}$$

Reparameterisation [32–34] has been performed. The objective function is minimised by applying the standard nonlinear least-square estimation technique, c.q., Gauss–Newton algorithm [35,36]. The parameter estimation has also been carried out through a Bayesian technique for parameter estimation [37] and leads to quasi-identical results. The software package used for the purpose is Greg Pak solvers of Athena visual work bench [38]. During regression, the statistical significance of the regression is expressed by means of the F-test, comparing the sum of squares of the calculated response values and the residual sum of squares. The individual significance of the parameters on the 95% probability level is tested using Students t-value.

3. Langmuir description of physisorption of alkanes on ZSM-22

The Langmuir isotherm for physisorption of a pure component i is based on the following site balance

$$C_i^{\mathrm{sat}} = C_{\mathrm{e}} + C_i \tag{3.1}$$

and is expressed as

$$C_i = \frac{K_{\mathrm{L},i} C_i^{\mathrm{sat}} p_i}{1 + K_{\mathrm{L},i} p_i}, \tag{3.2}$$

where C_i^{sat} is the saturation concentration of component i on the sorbent. For low partial pressures of component i, i.e., $K_{\mathrm{L},i} p_i \ll 1$, Eq. (3.2) is reduced to Eq. (2.1), valid in the Henry regime. Hence, the following relationship is obtained:

$$H_i = K_{\mathrm{L},i} C_i^{\mathrm{sat}}. \tag{3.3}$$

The Langmuir physisorption equilibrium coefficient for an alkane on a zeolite can be determined from the corresponding Henry coefficient and saturation concentration by applying Eq. (3.3). A Langmuir isotherm corresponds to monolayer formation. On ZSM-22, due to the molecular dimensions of micropores, multilayer formation does not occur inside the micropores. At the pore mouths multilayer formation is theoretically possible. However, it is expected that the forces involved in the multilayer formation are much weaker than the interactions of the sorbate with the pore mouth, preventing multilayer formation also at the pore mouth. Therefore, a Langmuir expression can be applied to describe the physisorption on ZSM-22 at low coverage [4–6] when physisorption is found to occur preferentially on the Brönsted acid sites [6,18,39], which are at pore mouths and inside the micropores for ZSM-22. It has been observed that at higher alkane partial pressures physisorption also occurs at the external crystal surfaces [6,9,19]. Under such conditions, the physisorption phenomenon can be described by a dual physisorption site model [6,9,19] with one type of physisorption site corresponding to the pore and pore mouth and another corresponding to the external surface. At lower alkane partial pressures, the effects of external surface physisorption can be neglected, as the physisorption equilibrium coefficients for micropores and pore mouths are significantly higher than the physisorption equilibrium coefficient for the external surface [6,9,19].

On ZSM-22 a distinction has to be made between the pore mouths and the micropores. Iso-alkanes, due to their bulkiness, are sterically hindered to physisorb inside the micropores and, hence, physisorb only at the pore mouths. *n*-Alkanes physisorb at the pore mouth and subsequently can enter the corresponding micropore. Additional enthalpy and entropy loss occurs when *n*-alkanes are transferred from pore mouths to micropores. As a result, a two-step physisorption model is developed for *n*-alkanes physisorbing inside the micropores, while a single-step physisorption describes the physisorption of iso-alkanes at the pore mouths, viz. Fig. 2.

3.1. *n*-Alkanes

n-Alkanes first physisorb at the pore mouths and further enter the micropore:

$$P_j + S_{\mathrm{e,pm}} \overset{K_{j,\mathrm{pm}}}{\rightleftarrows} P_{j,\mathrm{pm}},$$

$$P_{i,\mathrm{pm}} + S_{\mathrm{e,mp_l}} \overset{K_{\mathrm{pm-mp}}}{\rightleftarrows} P_{j,\mathrm{mp}}.$$

For a pure *n*-alkane "j" the equilibrium concentration at the pore mouth is given by

$$C_{j,\mathrm{pm}} = K_{j,\mathrm{pm}} C_{\mathrm{e,pm}} p_j. \tag{3.4}$$

A separate index j is used because exclusively *n*-alkanes are considered, whereas the index i in the previous section covers both normal and iso-alkanes. From the pore mouth an *n*-alkane can enter the micropore connected to that pore mouth. Due to the narrow micropore channels, the transport inside the micropore occurs via single-file diffusion. In single-file diffusion, the transfer into the micropore takes place via a series of activated site jumps [24]. The rate of this transfer is proportional to the concentration of alkane at pore mouth $C_{j,\mathrm{pm}}$ and the probability of finding an empty neighbouring micropore site $\hat{p}_{\mathrm{e,mp}}$ while the rate of transfer from the micropore to the pore mouth is proportional to the alkane concentration in the micropores, $C_{j,\mathrm{mp}}$, and the probability of the pore mouth being empty $\hat{p}_{\mathrm{e,pm}}$. Considering the transfer between pore mouth and micropore as being quasi-equilibrated, the alkane concentrations in the micropores can be expressed as follows:

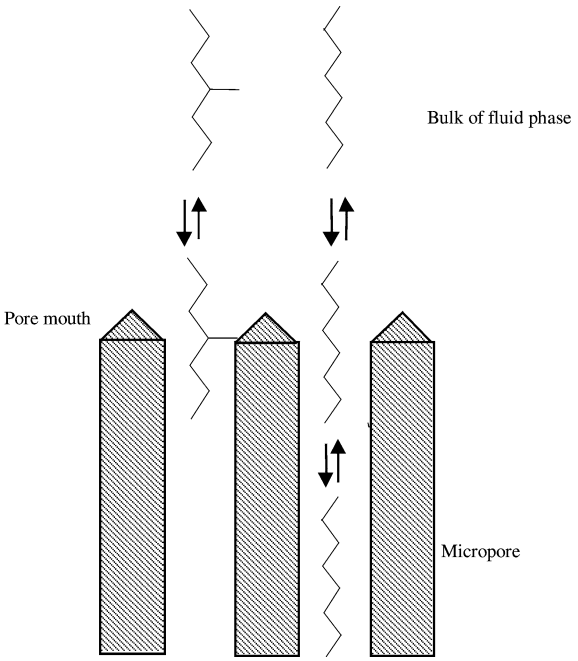


Fig. 2. Schematic representation of physisorption of *n*-alkanes and iso-alkanes on open ZSM-22.

$$\begin{aligned} C_{j,\mathrm{mp}} &= K_{\mathrm{pm-mp}} C_{j,\mathrm{pm}} \frac{\hat{p}_{\mathrm{e,mp}}}{\hat{p}_{\mathrm{e,pm}}} \\ &= K_{j,\mathrm{pm}} K_{\mathrm{pm-mp}} p_j C_{\mathrm{e,pm}} \frac{\hat{p}_{\mathrm{e,mp}}}{\hat{p}_{\mathrm{e,pm}}}. \end{aligned} \tag{3.5}$$

Assuming uniform site strength, viz. unbiased physisorption, probabilities for finding the empty sites can be expressed as

$$\hat{p}_{\mathrm{e,pm}} = \frac{C_{\mathrm{e,pm}}}{C_{\mathrm{t,pm}}}, \tag{3.6}$$

$$\hat{p}_{\mathrm{e,mp}} = \frac{C_{\mathrm{e,mp}}}{C_{\mathrm{t,mp}}}. \tag{3.7}$$

Substituting the above Eqs. (3.6) and (3.7) into Eq. (3.5),

$$C_{j,\mathrm{mp}} = K_{j,\mathrm{pm}} \left(K_{\mathrm{pm-mp}} \frac{C_{\mathrm{t,pm}}}{C_{\mathrm{t,mp}}} \right) p_j C_{\mathrm{e,mp}}. \tag{3.8}$$

A site balance for the micropore physisorption sites leads to

$$C_{t,mp} = C_{j,mp} + C_{e,mp}, \tag{3.9}$$

where $C_{t,mp}$ is the total number of physisorption sites in the micropores and corresponds to C_i^{sat} because the number of pore mouths is negligibly small. After solving Eq. (3.9) for $C_{e,mp}$ and substituting in Eq. (3.8), the Langmuir expression for physisorption of n-alkane j inside the micropores of ZSM-22 is written as

$$C_{j,mp} = \frac{K_{j,pm} K_{pm-mp}^{app} C_j^{sat} p_j}{1 + K_{j,pm} K_{pm-mp}^{app} p_j}, \tag{3.10}$$

where

$$K_{pm-mp}^{app} = K_{pm-mp} \frac{C_{t,pm}}{C_{t,mp}}. \tag{3.11}$$

Comparing the above expression with Eq. (3.2), it can be seen that the Langmuir equilibrium coefficient for physisorption of n-alkanes can be expressed as

$$K_{L,j} = K_{j,pm} K_{pm-mp}^{app}. \tag{3.12}$$

$K_{L,j}$ can be obtained from the experimentally measured Henry coefficient and the saturation concentration on open ZSM-22 using Eq. (3.3). Physisorption experiments on closed ZSM-22 allows calculation of the pore mouth physisorption, coefficient $K_{j,pm}$, because the subsequent transfer into the micropores after physisorption at the pore mouth is absent. The equilibrium coefficient for transfer between the pore mouth and the micropore, K_{pm-mp}, can then be obtained via Eqs. (3.11) and (3.12). From the temperature dependence of $K_{L,j}$ and $K_{j,pm}$ the standard physisorption enthalpy and entropy on open ZSM-22, $\Delta H_{j,mp}^{\circ}$ and $\Delta S_{j,mp}^{\circ}$ and on closed ZSM-22, $\Delta H_{j,pm}^{\circ}$ and $\Delta S_{j,pm}^{\circ}$ can be determined. $\Delta H_{j,mp}^{\circ}$ and $\Delta S_{j,mp}^{\circ}$ follow the carbon number dependency relationships for n-alkanes described by Eqs. (2.3) and (2.4), respectively. Based on Eqs. (3.11) and (3.12), the following relationship between the standard physisorption enthalpies on open and closed ZSM-22 can be written

$$\Delta H_{j,mp}^{\circ} = \Delta H_{j,pm}^{\circ} + \Delta H_{pm-mp}^{\circ}, \tag{3.13}$$

$$\Delta H_{pm-mp}^{app} = \Delta H_{pm-mp}^{\circ}. \tag{3.14}$$

A similar relationship holds for the physisorption entropies:

$$\Delta S_{j,mp}^{\circ} = \Delta S_{j,pm}^{\circ} + \Delta S_{pm-mp}^{\circ}, \tag{3.15}$$

$$\Delta S_{pm-mp}^{app} = \Delta S_{pm-mp}^{\circ} + R \ln\left(\frac{C_{t,pm}}{C_{t,mp}}\right). \tag{3.16}$$

As a result, the standard enthalpy and entropy loss upon transfer from the pore mouth to the micropore can be calculated from the difference between the standard physisorption enthalpies and entropies on open and closed ZSM-22 using Eqs. (3.13) to (3.16). The standard physisorption enthalpy ΔH_{pm-mp}° corresponds to the observed value of $-19.6\ \mathrm{kJ\,mol^{-1}}$ [18]. The observed standard physisorption entropy ΔS_{pm-mp}^{app} of $-89.33\ \mathrm{J\,mol^{-1}\,K^{-1}}$ [18] is actually not the true standard physisorption entropy for pore mouth–micropore transfer as it also contains the factor $C_{t,pm}/C_{t,mp}$, viz. Eq. (3.16). Accounting for this factor, viz., Table 1, the true standard physisorption entropy ΔS_{pm-mp}° is calculated as $-27.8\ \mathrm{J\,mol^{-1}\,K^{-1}}$.

3.2. Iso-alkanes

The physisorption of pure iso-alkane “k” on ZSM-22 only occurs at the pore mouths:

$$P_k + S_{e,pm} \overset{K_{k,pm}}{\rightleftarrows} P_{k,pm}.$$

This leads to the following Langmuir expression for iso-alkane physisorption at the pore mouth:

$$C_{k,pm} = \frac{K_{k,pm} C_{t,pm} p_k}{1 + K_{k,pm} p_k}. \tag{3.17}$$

Comparing the above expression with Eq. (3.2), it can be seen that the Langmuir coefficient for iso-alkane k, $K_{L,k}$, corresponds to $K_{k,pm}$ while the saturation concentration for an iso-alkane k, C_k^{sat}, corresponds to $C_{t,pm}$. $K_{k,pm}$ is obtained from the ratio of the experimentally measured Henry coefficient and the saturation concentration, viz. Eq. (3.3). The above discussion holds for both open and closed ZSM-22 because on both forms iso-alkanes physisorb at the pore mouths only.

4. Modes of physisorption for alkanes on ZSM-22

An iso-alkane at the pore mouth can physisorb in different orientations, leading to multiple physisorption modes, viz. Fig. 3. Inside the micropores strong force fields exist and, hence, interactions with the crystal lattice occur for carbon atoms inside the micropore. For n-alkanes, all of the carbon atoms are subject to such interactions. For iso-alkanes, these interactions are limited to the portion of the molecule protruding inside the pore mouth and are directly proportional to the number of carbon atoms protruding into the pore mouth. However, apart from the interactions experienced by carbon atoms protruding inside the pore mouth, the carbon

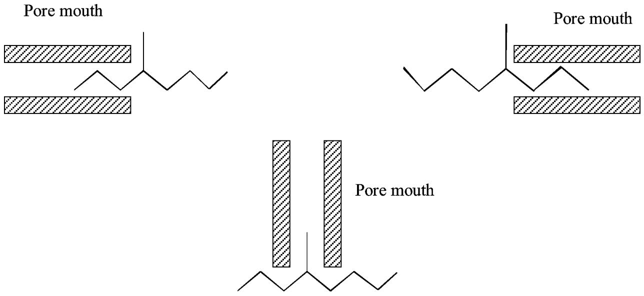


Fig. 3. Schematic representation of the three possible physisorption modes of 4-methyloctane at a ZSM-22 pore mouth indicated by parallel rectangular blocks.

atoms outside the pore mouth also experience energetic interactions with the crystal lattice, albeit to a lesser extent.

Each physisorption mode is characterised by the number of carbon atoms inside and outside the pore mouth. The number of pore mouth physisorption modes corresponds to the number of straight ends in the molecule. In each of the pore mouth physisorption modes one of the straight ends of the molecule protrudes into the pore mouth, while the remaining portion of the molecule is outside. The relative distribution of all existing modes depends on the energetic interactions in these modes.

Fig. 3 is an illustration of the different pore mouth physisorption modes for 4-methyloctane (4MeC8). This iso-alkane has three straight ends and, hence, in a pore mouth configuration there are three physisorption modes with any one of the straight ends inside the micropore and others outside the micropore. The Henry coefficients for iso-alkanes discussed in the previous section correspond to a composite value over all possible physisorption modes. For n-alkanes the observed physisorption behavior can be related to a single physisorption mode, i.e., with all carbon atoms inside the micropore. Hence, for n-alkanes the Henry coefficient is obtained by Eq. (2.2) along with Eqs. (2.3) and (2.4) using the standard physisorption enthalpy and entropy inside the micropore. In the calculation of the Henry coefficients for the iso-alkanes each of the possible physisorption modes has to be accounted for. The composite Henry coefficient for 4-methyloctane consists of the Henry coefficients of its three individual physisorption modes, viz. Fig. 3:

$$P_k + S_{\mathrm{e,pm}} \overset{K_{k_m,\mathrm{pm}}}{\rightleftarrows} P_{k_m,\mathrm{pm}}$$

(for straight end m inside the pore mouth cavity).

Considering the following site balance at pore mouths,

$$C_{\mathrm{t,pm}} = C_{\mathrm{e,pm}} + \sum_{m=1}^{3} C_{k_m,\mathrm{pm}} \tag{4.1}$$

and

$$C_{k_m,\mathrm{pm}} = K_{k_m,\mathrm{pm}} p_k C_{\mathrm{e,pm}}, \tag{4.2}$$

where $C_{k_m,\mathrm{pm}}$ is the concentration of the physisorption mode m and $K_{k_m,\mathrm{pm}}$ is the equilibrium constant for physisorption in mode m. The Langmuir expression for individual physisorption mode (Eq. (2.2)) can be written as follows:

$$C_{k_m,\mathrm{pm}} = \frac{K_{k_m,\mathrm{pm}} C_{\mathrm{t,pm}} p_k}{1 + \sum_{m=1}^{3} K_{k_m,\mathrm{pm}} p_k}. \tag{4.3}$$

The total concentration of physisorbed alkanes k at pore mouths is expressed as

$$\begin{aligned} C_{k,\mathrm{pm}} &= \sum_{m=1}^{3} C_{k_m,\mathrm{pm}} = \sum_{m=1}^{3} \frac{K_{k_m,\mathrm{pm}} C_{\mathrm{t,pm}} p_k}{1 + \sum_{m=1}^{3} K_{k_m,\mathrm{pm}} p_k} \\ &= \frac{\left(\sum_{m=1}^{3} K_{k_m,\mathrm{pm}}\right) C_{\mathrm{t,pm}} p_k}{1 + \left(\sum_{m=1}^{3} K_{k_m,\mathrm{pm}}\right) p_k}. \end{aligned} \tag{4.4}$$

Extending Eqs. (4.1)–(4.4) to any alkane having N pore mouth physisorption modes leads to

$$K_{k,\mathrm{pm}} = \sum_{m=1}^{N} K_{k_m,\mathrm{pm}}. \tag{4.5}$$

Multiplying both sides of Eq. (4.5) with the saturation concentration C_k^{sat}, which corresponds to the concentration of pore mouths $C_{\mathrm{t,pm}}$ and using the relationship between the Henry coefficient and Langmuir physisorption equilibrium coefficient, viz. Eq. (3.3), the Henry coefficient for iso-alkane can be expressed in terms of "Henry coefficients" for individual modes of physisorption at pore mouths as

$$H_{k,\mathrm{pm}} = \sum_{m=1}^{N} H_{k_m,\mathrm{pm}}. \tag{4.6}$$

Hence, when multiple physisorption modes exist, the observable Henry coefficient for physisorption is a "composite," which equals the sum of the Henry coefficients of the individual physisorption modes. The latter Henry coefficients can be calculated using correlations for physisorption enthalpy and entropy given in the next section. The above treatment for pore mouth physisorption modes is expected to be extendable to key-lock physisorption modes, which is, however, beyond the scope of the present paper.

For iso-alkanes, experimental values of the composite Henry coefficient for pore mouth physisorption can be obtained from classical physisorption experiments on ZSM-22. For n-alkanes the same can be obtained from such experiments on closed ZSM-22. It will be evident from the subsequent discussions that a major advantage of distinguishing between different physisorption modes is the possibility to come to a uniform set of parameters to describe the physisorption properties of all alkane classes, instead of different parameter sets required now for each alkane class, e.g., 2-methylalkanes, 3-methylalkanes, etc. [4–6,18].

4.1. Standard physisorption enthalpy

The standard physisorption enthalpy for a given physisorption mode of an iso-alkane k at a pore mouth of ZSM-22, $\Delta H^\circ_{k_m,\mathrm{pm}}$, consists of several contributions. As explained in Section 2.3, enthalpy losses occur via the carbon atoms inside and outside the pore mouth:

$$\Delta H^\circ_{k_m,\mathrm{pm}} = \Delta H^\circ_{\mathrm{CNP}_{k_m}} + \Delta H^\circ_{\mathrm{CNO}_{k_m}}. \tag{4.7}$$

The enthalpy loss of the carbon atoms inside the pore mouth cavity is calculated using Eq. (2.3) with the number of carbon atoms inside the pore mouth, CNP_{k_m}, instead of the total number of carbon atoms of the physisorbing iso-alkane. This allows use of the values for the parameters α and β obtained from physisorption experiments on n-alkanes on open ZSM-22 [4,6,18], viz. Table 2, to calculate $\Delta H^\circ_{\mathrm{CNP}_{k_m}}$ for any alkane at the pore mouths after accounting for the enthalpy loss upon transfer of n-alkanes from the pore mouth to the micropore, $\Delta H^{\circ}_{\mathrm{pm-mp}}$ viz. Eq. (3.13). This leads to the following expression for the iso-alkane physisorption enthalpy in mode m:

$$-\Delta H^{\circ}_{\mathrm{CNP}_{k_m}} = \alpha \mathrm{CNP}_{k_m} + \beta - \Delta H^{\circ}_{\mathrm{pm-mp}}. \tag{4.8}$$

The enthalpy loss corresponding to interactions of carbon atoms outside the pore mouth cavity is considered to consist of two terms:

$$-\Delta H^{\circ}_{\mathrm{CNO}_{k_m}} = \alpha^{\mathrm{o}} \mathrm{CNO}_{k_m} + \beta^{\mathrm{o}}. \tag{4.9}$$

In the above equation, α^{o} corresponds to the average enthalpy loss per carbon atom due to carbon atoms outside. Next to this linear contribution, the second term β^{o} accounts for structural differences in the alkyl chains interacting with the external crystal surface and in particular allows accounting for the degree of branching of the alkyl chains. Indeed, these interactions vary with degree of branching. The interactions of monobranched alkanes with the external crystal lattice are stronger than multibranched alkanes. Also, in the case of multibranched alkanes with tertiary carbon atoms different tertiary carbon atoms are at the pore mouth in different physisorption modes, while monobranched alkanes have the same tertiary carbon atom interacting with the pore mouth in all its physisorption modes. This also contributes to the differences in energetic interactions. The differences in energetic interactions of monobranched and multibranched alkanes are accounted for by considering separate parameters: $\beta^{\mathrm{o}}_{\mathrm{mo}}$, which accounts for interactions of monobranched alkanes, and $\beta^{\mathrm{o}}_{\mathrm{ml}}$, which accounts for interactions of multibranched alkanes.

4.2. Standard physisorption entropy

The standard physisorption entropy for every individual physisorption mode, $\Delta S^{\circ}_{k_m,\mathrm{pm}}$, can be expressed in similar terms as the standard physisorption enthalpy. For a given physisorption mode of iso-alkane k at a pore mouth of ZSM-22, $\Delta S^{\circ}_{k_m,\mathrm{pm}}$, consists of a contribution, $\Delta S^{\circ}_{\mathrm{CNP}_{k_m}}$, due to carbon atoms inside the pore mouth cavity, and a contribution, $\Delta S^{\circ}_{\mathrm{CNO}_{k_m}}$, due to interactions of carbon atoms outside:

$$\Delta S^{\circ}_{k_m,\mathrm{pm}} = \Delta S^{\circ}_{\mathrm{CNP}_{k_m}} + \Delta S^{\circ}_{\mathrm{CNO}_{k_m}}. \tag{4.10}$$

Analogous to the loss in physisorption enthalpy discussed above, the loss in physisorption entropy due to carbon atoms inside the pore mouth, $\Delta S^{\circ}_{\mathrm{CNP}_{k_m}}$ is calculated using Eq. (2.4) with the values for the parameters γ and δ obtained from physisorption experiments on n-alkanes on open ZSM-22 [4,6,18], viz. Table 2, after accounting for the entropy difference between the pore mouth and micropore physisorption, i.e., $\Delta S^{\circ}_{\mathrm{pm-mp}}$, viz. Eq. (3.15). This leads to the following expression for the entropy loss due to the carbon atoms inside the pore mouth for the iso-alkane physisorbed in mode m:

$$-\Delta S^{\circ}_{\mathrm{CNP}_{k_m}} = \gamma \mathrm{CNP}_{k_m} + \delta - \Delta S^{\circ}_{\mathrm{pm-mp}}. \tag{4.11}$$

The analogy further extends to the carbon atoms outside. A linear relationship between the entropy loss due to the carbon atoms outside and the number of carbon atoms outside the pore mouth is proposed and is expressed as follows for a given physisorption mode m:

$$-\Delta S^{\circ}_{\mathrm{CNO}_{k_m}} = \gamma^{\mathrm{o}} \mathrm{CNO}_{k_m} + \delta^{\mathrm{o}}. \tag{4.12}$$

γ^{o} corresponds to the average entropy loss per carbon atom due to carbon atoms outside the pore mouth and δ^{o} accounts for the differences in interactions with crystal lattice between mono- and multibranched alkanes: $\delta^{\mathrm{o}}_{\mathrm{mo}}$, for monobranched alkanes, and $\delta^{\mathrm{o}}_{\mathrm{ml}}$, for multibranched alkanes.

5. Parameter estimation

5.1. Model equations

Eq. (2.2) enables the calculation of the Henry coefficients from the standard physisorption enthalpy and entropy [4–6] and is applicable for individual physisorption modes. Eq. (4.6) allows calculation of the observable composite Henry coefficient as the sum of the Henry coefficients of the individual physisorption modes. This is expressed in terms of standard physisorption enthalpies and entropies of individual physisorption modes as follows,

$$H_{k,\mathrm{pm}} = \left(\frac{C_{\mathrm{t,pm}}}{2p^{\circ}}\right) \sum_{m} \mathrm{e}^{\Delta S^{\circ}_{k_m,\mathrm{pm}}/R} \mathrm{e}^{-\Delta H^{\circ}_{k_m,\mathrm{pm}}/(RT)}, \tag{5.1}$$

where $\Delta H^{\circ}_{k_m,\mathrm{pm}}$ is obtained from Eqs. (4.7) to (4.9) and $\Delta S^{\circ}_{k_m,\mathrm{pm}}$ from Eqs. (4.10) to (4.12). The contributions to the standard physisorption enthalpy and entropy loss via the carbon atoms protruding inside the pore mouth are calculated using the α, β, γ, and δ values reported in Table 2. The contributions to the standard physisorption enthalpy and entropy loss via the carbon atoms outside the pore mouths given by Eqs. (4.9) and (4.12), respectively, are determined via regression of experimental data. The experimental data set, viz. Table 1, contains physisorption properties of normal and branched alkanes with 5–9 carbon numbers. As explained in Section 2.3, alkanes having only pore mouth physisorption modes have been considered for regression. A composite Henry coefficient for pore mouth physisorption has also been calculated for the iso-alkanes, exhibiting key-lock physisorption modes, i.e., 2MeC7, 2MeC8, and 3MeC8. Comparison of these values with the observed Henry coefficients allows estimation of the relative importance between pore mouth and key-lock physisorption modes.

5.2. Regression results

Based on the discussions in the preceding sections, six parameters are to be estimated: α^{o}, $\beta^{\mathrm{o}}_{\mathrm{mo}}$, $\beta^{\mathrm{o}}_{\mathrm{ml}}$, γ^{o}, $\delta^{\mathrm{o}}_{\mathrm{mo}}$, and $\delta^{\mathrm{o}}_{\mathrm{ml}}$ from the regression of the experimental data. The parameter estimates along with their individual approximate

Table 3
Estimates with their 95% confidence intervals for the parameters of Eqs. (4.9) and (4.12) obtained through regression of the model based on multiple physisorption modes (Eq. (5.1) along with Eqs. (4.7) to (4.12)) and experimental data sets for open ZSM-22 [4,5,18], viz. Table 1

Parameter	Estimated value (95% confidence limits)
α^o (kJ mol^{-1})	6.89 (±1.44)
γ^o (J mol^{-1} K^{-1})	8.97 (±2.17)
β^o_{mo} (kJ mol^{-1})	30.14 (±2.34)
δ^o_{mo} (J mol^{-1} K^{-1})	−2.60 (±2.40)
β^o_{ml} (kJ mol^{-1})	9.02 (±2.91)
δ^o_{ml} (J mol^{-1} K^{-1})	−27.80 (±1.30)

Parameter values for Eqs. (4.8) and (4.11) from Table 2.

95% confidence intervals are reported in Table 3. These confidence intervals correspond to t values in the range 10^1 to 10^2. As expected, the enthalpy and entropy loss per carbon atom due to interactions outside the pore mouth, α^o and γ^o, are lower than the enthalpy and entropy loss per carbon atom inside the pore mouth. The constant standard physisorption enthalpy and entropy loss are higher for monobranched alkanes than for multibranched alkanes, i.e., $\beta^o_{mo} > \beta^o_{ml}$ and $\delta^o_{mo} > \delta^o_{ml}$, which is considered to be the result from a more favourable interaction of monobranched alkanes with the zeolite lattice than multibranched alkanes. The difference between β^o_{mo} and β^o_{ml} is 21.1 kJ mol^{-1} and that between δ^o_{mo} and δ^o_{ml} is 25.2 J mol^{-1} K^{-1}, which is close to the typically observed experimental differences. For example, 3-methylpentane in its most favourable physisorption mode has two carbon atoms protruding inside the pore mouth cavity. The enthalpy loss for this mode is observed to be 61.7 kJ mol^{-1}. For 2,2-dimethylbutane, which also has same number of carbon atoms protruding inside the pore mouth cavity in its most favourable physisorption mode, the enthalpy loss is observed as 38.7 kJ mol^{-1}. A difference in the interactions of 23 kJ mol^{-1} exists between these two molecules, even though they have the same number of carbon atoms inside the pore mouth and outside. Similarly, the difference in entropy loss is observed as 31 J mol^{-1} K^{-1}. The F value for the significance of the regression amounts to 4500, indicating a high global significance of regression. Binary correlation between the estimates is very low. The highest absolute value of the binary correlation coefficient was observed between $\beta^o_{ml} - \delta^o_{ml}$ and amounts to 0.29. Table 4 shows a comparison of calculated Henry coefficients with experimental data at 573 K. Henry coefficients calculated by CBMC [20] are also shown. They are found to underpredict the experimental data. Fig. 4 shows the parity diagram of the Henry coefficients at various temperatures for all the normal and monobranched alkanes. The calculated composite pore mouth Henry coefficients for 2MeC8, 3MeC8, and 2MeC7 are approximately 20% lower than the experimentally obtained Henry coefficients. This indicates that about 20% of 2MeC8, 3MeC8, and 2MeC7 physisorb in a key-lock mode. For multibranched alkanes only, the F value obtained during regression is 650. Henry coefficients for multibranched alkanes having quaternary carbon atoms are closely estimated with a systematic small overprediction within 5%. The Henry coefficients for multibranched

Table 4
Henry coefficients (H) (mol kg^{-1} Pa^{-1}) for alkanes on open ZSM-22 at 573 K: a comparison between estimates obtained from the model during regression using Eq. (5.1) along with Eqs. (4.7) to (4.12) and experimental data set of open ZSM-22 [4,5,18]), viz. Table 1

Alkanes	Experimental [4,5]	Model based on multiple physisorption modes	Based on CBMC [20]
nC5	1.32	1.33	0.65
2MeC4	0.32	0.32	0.12
nC6	2.59	2.54	1.43
2MeC5	0.54	0.52	0.23
3MeC5	0.44	0.50	0.18
22DMC4	0.13	0.15	1.80×10^{-9}
23DMC4	0.23	0.14	7.42×10^{-3}
nC7	4.66	4.87	2.81
2MeC6	1.13	0.86	0.67
3MeC6	0.87	0.82	0.34
23DMC5	0.42	0.21	0.02
33DMC5	n.a.[b]	0.22	5.98×10^{-10}
nC8	8.82	9.33	n.a.[b]
2MeC7[a]	2.04	1.47	n.a.
3MeC7	1.50	1.34	n.a.
4MeC7	1.45	1.30	n.a.
25DMC6	0.63	0.28	n.a.
224TMC5	0.30	0.36	n.a.
nC9	19.0	17.8	n.a.
2MeC8[a]	3.80	2.50	n.a.
3MeC8[a]	3.50	2.22	n.a.

Parameter values for Eqs. (4.8) and (4.11) from Table 2 and Eqs. (4.9) and (4.12) from Table 3.

[a] Not included in parameter estimation as they also contain key-lock modes of physisorption.

[b] n.a.: not available.

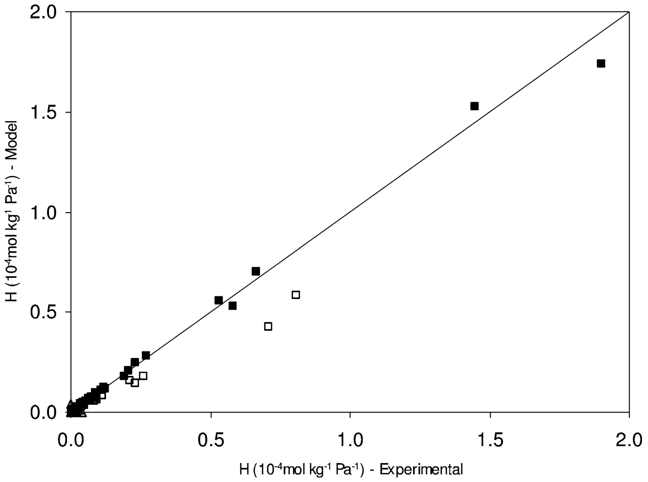


Fig. 4. Henry coefficients (mol kg^{-1} Pa^{-1}) for normal and monobranched C5–C9 alkanes at temperatures 473–673 K. A comparison between experimental data on open ZSM-22 [4–6] and model regression based on multiple physisorption modes using Eq. (5.1). Line, experimental; symbols, calculated. The open symbols correspond to the molecules having also key-lock physisorption modes. Parameter values for Eqs. (4.8) and (4.11) are from Table 2 and for Eqs. (4.9) and (4.12) from Table 3.

Table 5
Molar equilibrium fractions for the physisorption modes of 3-methylheptane calculated from molar concentrations obtained using Eqs. (4.3) and (4.4) along with Eqs. (4.7) to (4.12)

Physisorption mode m	CNP_k^m	x_{k_m}	$-\Delta H^\circ_{k_m,\mathrm{pm}}$ (kJ mol^{-1})	$-\Delta S^\circ_{k_m,\mathrm{pm}}$ (J mol^{-1} K^{-1})
1	4	0.50	87.2	102.3
2	2	0.29	75.3	86.3
3	1	0.21	69.4	78.3

Parameter values for Eqs. (4.8) and (4.12) from Table 2 and Eqs. (4.9) and (4.12) from Table 3.

alkanes with tertiary carbon atoms are underestimated by 30–40%. This indicates that multibranched alkanes with tertiary carbon atoms interact more strongly with the external crystal lattice than multibranched alkanes with quarternary carbon atoms.

The composite standard physisorption enthalpy and entropy have been calculated from the enthalpies and entropies for the individual physisorption modes using the following mixing rule:

$$\Delta H^\circ_{k,\mathrm{pm}} = \sum_{m=1}^{N} x_{k_m} \Delta H^\circ_{k_m,\mathrm{pm}}, \tag{5.2}$$

$$\Delta S^\circ_{k,\mathrm{pm}} = \sum_{m=1}^{N} x_{k_m} \Delta S^\circ_{k_m,\mathrm{pm}} - R \sum_{m=1}^{N} x_{k_m} \ln x_{k_m}, \tag{5.3}$$

where x_{k_m} is the equilibrium mole fraction of individual mode m within the mixture of possible pore mouth physisorption modes for iso-alkane k. It is calculated from the molar concentration of each of these modes obtained from Eq. (4.3). $\Delta H^\circ_{k_m,\mathrm{pm}}$ is the standard physisorption enthalpy for each individual mode calculated using Eqs. (4.7) to (4.9) and $\Delta S^\circ_{k_m,\mathrm{pm}}$ is the standard physisorption entropy for each individual mode calculated from Eqs. (4.10) to (4.12). The calculated molar equilibrium fractions and the enthalpy and entropy losses for the three physisorption modes of 3-methylheptane, viz. Table 5, lead to a composite standard physisorption enthalpy of -80 kJ mol^{-1} and a composite standard physisorption entropy of -84 J mol^{-1} K^{-1}, which is close to the experimentally observed values of -84 kJ mol^{-1} and -84 J mol^{-1} K^{-1} [5,6,18]. From the molar distribution it is clear that the most favoured physisorption state is the one which has maximum carbon atoms protruding inside the pore mouth cavity. For 3-methylheptane it corresponds to the physisorption mode with four carbon atoms protruding inside the pore mouth cavity, which has an equilibrium mole fraction of 0.5. This is the physisorption mode with the maximum enthalpy and entropy loss. The calculated composite pore mouth physisorption enthalpies for all alkanes correspond well with the experimentally obtained values [4–6,18], viz. Fig. 5. The same quality of correspondance has been observed between the calculated and the experimentally determined entropies. Fig. 6 shows the estimated physisorption enthalpy for n-octane and some of its isomers. The model describes the variations in physisorption enthalpies of the normal and iso-alkanes. n-Octane has the highest enthalpy loss as all the eight carbon atoms are inside the micropore. 2-Methylheptane has the next highest enthalpy loss as in its most favoured physisorption mode five carbon atoms are protruding into the pore mouth cavity. This is followed by 3-methyl- and 4-methylheptanes. The multibranched alkanes have the lowest enthalpy loss as their interactions with the poremouth and external crystal lattice are weaker.

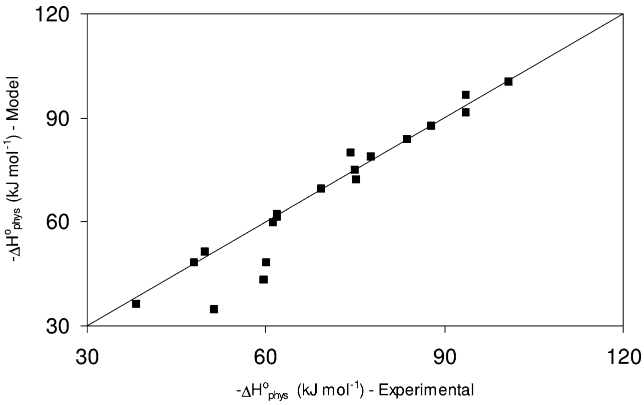


Fig. 5. Composite standard physisorption enthalpy (kJ mol^{-1}) of C5–C9 alkanes. A comparison between experimental data on open ZSM-22 [4–6] values obtained using an ideal mixing rule (Eq. (5.2) along with Eqs. (4.3), (4.4), and (4.7) to (4.9)) considering standard physisorption enthalpy for individual physisorption modes. Line, experimental; symbols, calculated. Parameter values for Eqs. (4.8) and (4.11) are from Table 2 and for Eqs. (4.9) and (4.12) from Table 3.

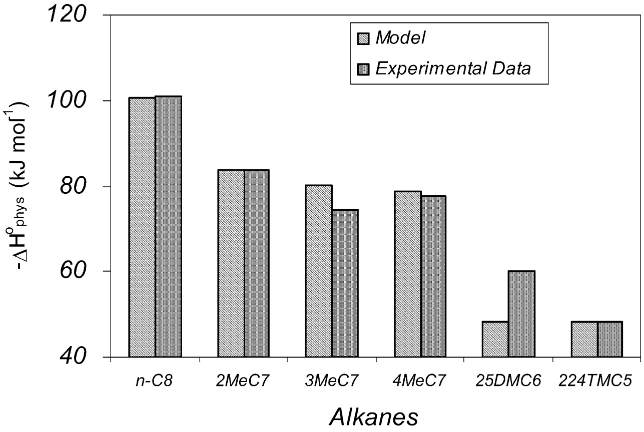


Fig. 6. Composite standard physisorption enthalpy (kJ mol^{-1}) of C8 alkanes. A comparison between experimental data on open ZSM-22 [4–6] and calculated values using Eq. (5.2) along with Eqs. (4.3), (4.4), and (4.7) to (4.9). Parameter values for Eqs. (4.8) and (4.11) are from Table 2 and for Eqs. (4.9) and (4.12) from Table 3.

6. Effect of physisorption on the kinetics of hydrocarbon conversion on ZSM-22

On wide pore zeolites such as USY, normal and iso-alkanes can enter the micropores completely. As a result,

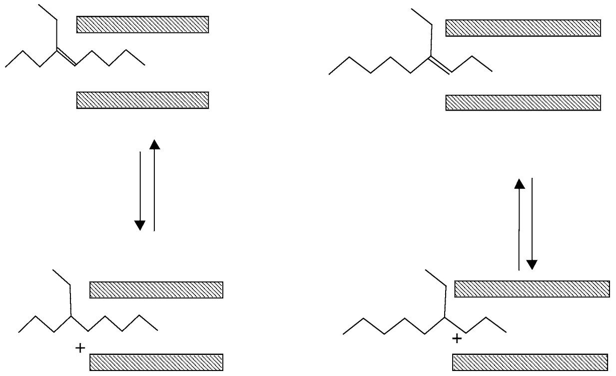


Fig. 7. Schematic representation of chemisorption of 4-ethylnon-4-ene and 4-ethylnon-3-ene on a ZSM-22 pore mouth.

there is only one physisorption mode for all alkanes on USY. For a given carbon number, the standard physisorption enthalpies and entropies and, hence, the physisorption equilibrium coefficients are comparable for n-alkanes and iso-alkanes [4–6]. Subsequent alkene chemisorption on the acid sites inside the micropores occurs without restriction and, hence, all reactions of the full reaction network occur [40]. As a result, the product distribution on USY is mainly governed by the full reaction network kinetics and physisorption effects are uniform for all molecules with the same carbon number. For n-octane hydroconversion on Pt-H-USY 3-methylheptane is the most abundantly formed isomer followed by 2-methylheptane and 4-methylheptane [40].

In contrast to USY, on ZSM-22, physisorption effects are nonuniform for molecules with the same carbon number, which significantly affects the acid-catalysed reactions subsequent to physisorption. The pore mouth physisorption on ZSM-22 leads to different physisorption modes with a different standard physisorption enthalpy, entropy, and, hence, Henry coefficient. As a result, the physisorbed alkanes are not equally distributed over the different modes. As described in Section 5.2, the distribution over the different physisorption modes is such that the physisorption mode with the highest number of carbon atoms inside the pore mouth occurs in abundance. For example, among the octane isomers the 2-methylheptane having the longest straight end in one of its modes has the highest concentration. Hydroconversion reactions of alkanes proceed via alkene and carbenium ion intermediates. (De)-hydrogenation and (de)-protonation reactions in this case are fast compared to skeletal isomerisation and cracking and are generally considered to be quasi-equilibrated [40]. In pore mouth catalysis on ZSM-22, a carbenium ion is always formed at the pore mouth and, hence, the physisorption mode determines which carbenium ion can be formed; e.g., different physisorption modes are required for carbenium ion formation from 4-ethylnon-4-ene or from 4-ethylnon-3-ene, viz. Fig. 7. The concentration of a carbenium ion corresponding to an alkane physisorbed in a preferred mode will be relatively high and, hence, the acid-catalysed reactions in which such a carbenium ion is consumed proceed at higher rates than the reactions involving nonpreferentially formed carbenium ions. This is evident from the product distribution of n-octane hydroconversion on ZSM-22 where 2-methylheptane is the most abundant product followed by 3-methylheptane and 4-methylheptanes [9]. Product distribution in the same lines, e.g., 2-methylalkane > 3-methylalkane > 4-methylalkane, are observed for other alkanes [7,15].

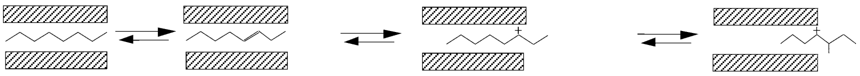
The above discussion can be extended to other acid-catalysed reactions, e.g., catalytic cracking. Even if the (de)-protonation reactions are not quasi-equilibrated, the preceding physisorption step can be assumed to be quasi-equilibrated. This leads to the distribution of the components involved over the different physisorption modes which can be calculated using the methodology developed in this work. Within the group of carbenium ions belonging to a particular physisorption mode, the hydride shift reactions, which are much faster than alkyl shift, PCP branching, and cracking reactions, are expected to lead to a quasi-equilibration [41]. Hence, higher concentrations of the carbenium ions belonging to the most favoured physisorption mode are still expected under these conditions.

Apart from the steric effects on the carbenium ions concentrations the reaction rates can also be affected by changes in physisorption during the course of reactions. For example, during the PCP isomerisation from a normal to an iso-alkane the reacting carbenium ion slightly moves outward from the pore mouth as shown in Scheme 1. These physisorption changes are again characterised by changes in the number of carbon atoms inside and outside the pore mouths. They result in changes in interactions between the reacting carbenium ion and the zeolite lattice during the course of an elementary reaction and, hence, in changes in physisorption enthalpy and entropy.

Compared to USY, the shape-selective effects on ZSM-22 affect the rates of the elementary acid-catalysed reactions and the resulting product distribution. The effects of physisorption on the kinetics can be quantified using the methodology discussed in the previous sections.

7. Conclusions

The physisorption of iso-alkanes on ZSM-22 result in their multiple pore mouth physisorption modes. Each of these modes is characterised by the number of carbon atoms of the molecule inside the pore mouth cavity and outside.



Scheme 1.

The enthalpy and entropy changes for carbon atoms outside the pore mouth are due to their energetic interactions with the crystal surface. These interactions vary for monobranched and multibranched alkanes. A two-step physisorption model distinguishing between physisorption at the pore mouths and subsequent transfer from the pore mouth to the micropore describes the physisorption phenomenon.

The observable Henry coefficient for pore mouth physisorption of alkanes is the sum of the Henry coefficients of the individual physisorption modes. An additivity approach using the properties of n-alkane physisorption on ZSM-22 adequately describes the physisorption properties of all given modes of iso- and normal alkanes. As each physisorption mode plays a distinct role in subsequent acid-catalysed reactions on ZSM-22, the calculation methodology of physisorption properties of individual physisorption modes will allow the description of kinetics on ZSM-22 in a fundamental way.

Acknowledgments

This research has been done as a part of the Interuniversitaire attractiepolen (IAP), funded by the Belgian government, Diensten van de Eerste Minister-Federale diensten voor wetenschappelijke, technishe en culturele aangelegenheden.

Appendix A. Nomenclature

A.1. Roman symbols

CN	Carbon number
CNP	Carbon atoms inside the pore
CNO	Carbon atoms outside the pore
C^{sat}	Saturation concentration ($\mathrm{mol\,kg_{cat}^{-1}}$)
C_i	Concentration of physisorbed alkane i ($\mathrm{mol\,kg_{cat}^{-1}}$)
C_{t}	Total concentration of physisorption sites ($\mathrm{mol\,kg_{cat}^{-1}}$)
C_{e}	Concentration of empty physisorption sites ($\mathrm{mol\,kg_{cat}^{-1}}$)
H	Henry's coefficient ($\mathrm{mol\,kg_{cat}^{-1}\,Pa^{-1}}$)
ΔH	Enthalpy change ($\mathrm{kJ\,mol^{-1}}$)
K_{L}	Langmuir physisorption equilibrium coefficient ($\mathrm{Pa^{-1}}$)
$K_{i,\mathrm{pm}}$	Physisorption coefficient at pore mouth for alkane i ($\mathrm{Pa^{-1}}$)
$K_{\mathrm{pm-mp}}$	Equilibrium coefficient for pore mouth–micropore transfer
P	Alkane species
p_i	Partial pressure of alkane i (Pa)
p°	Standard state pressure (Pa)
$\hat{p}_{\mathrm{e}}$	Probability of finding an empty site for physisorption
r	Rate of physisorption ($\mathrm{mol\,s^{-1}}$)
S	Physisorption sites
ΔS	Entropy change ($\mathrm{kJ\,mol^{-1}\,K^{-1}}$)
T	Temperature (K)
w	Weights for parameter estimation

A.2. Greek symbols

α	Physisorption enthalpy loss per carbon atom ($\mathrm{kJ\,mol^{-1}}$)
β	Constant physisorption enthalpy loss ($\mathrm{kJ\,mol^{-1}}$)
γ	Physisorption entropy loss per carbon atom ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
δ	Constant physisorption entropy loss ($\mathrm{J\,mol^{-1}\,K^{-1}}$)

A.3. Superscript

app	Apparant
c	Composite
exp	Experimental
m	Physisorption mode
$\circ$	Standard state
o	Parameters for carbon atoms outside the micropore
phys	Physisorption
sat	Saturation

A.4. Subscript

e	Empty physisorption sites
i	Index for alkanes
iso	Iso-alkanes
j	Index for experimental set
j	Index for n-alkane
k	Index for iso-alkane
L	Composite Langmuir physisorption equilibrium
m	Index for physisorption modes
ml	Multibranched alkanes
mo	Monobranched alkanes
mp	Micropore
np	n-Alkanes
phys	Physisorption
pm	Pore mouth
pm–mp	Pore mouth–micropore
t	Total physisorption sites

References

[1] I.E. Maxwell, W.H.J. Stork, in: H. Van Bekkum, E.M. Flanigen, J.C. Lansen (Eds.), in: Introduction to Zeolite Science and Practice, Vol. 58, Elsevier, Amsterdam, 1991, p. 571.

[2] J.A.Z. Pieterse, S.V. Reyes, K. Seshan, J.A. Lercher, J. Phys. Chem. B 104 (2000) 5715.

[3] Atlas of zeolite frame work types http://www.iza-structure.org/databases/.

[4] J.F.M. Denayer, G.V. Baron, P.A. Jacobs, J.A. Martens, J. Phys. Chem. B 102 (1998) 3077.

[5] J.F.M. Denayer, G.V. Baron, W. Souverijns, J.A. Martens, P.A. Jacobs, J. Phys. Chem. B 102 (1998) 4588.

[6] J.F.M. Denayer, Adsorption and reaction on zeolites: An integrated approach, PhD thesis, Vrije Universiteit, Brussel, 1998.
[7] J.A. Martens, R. Parton, L. Uytterhoeven, P.A. Jacobs, Appl. Catal. 76 (1991) 95.
[8] J.A. Martens, W. Souverijns, W. Verrelst, R. Parton, G.F. Froment, P.A. Jacobs, Angew. Chem. Int. Ed. Engl. 34 (1995) 2528.
[9] J.A. Martens, G. Vanbutsele, P.A. Jacobs, J.F.M. Denayer, R. Ocakoglu, G.V. Baron, J.A. Munoz Arroyo, J.W. Thybaut, G.B. Marin, Catal. Today 65 (2001) 111.
[10] R. Parton, L. Uytterhoeven, J.A. Martens, P.A. Jacobs, Appl. Catal. 76 (1991) 131.
[11] Van de Runstraat, J.A. Kamp, P.J. Stobbelaar, J. van Grondelle, S. Krijnen, R.A. van Santen, J. Catal. 171 (1997) 77.
[12] W. Souverijns, J.A. Martens, L. Uytterhoeven, G.F. Froment, P.A. Jacobs, Stud. Surf. Sci. Catal. 105 (1997) 1285.
[13] W. Souverijns, J.A. Martens, G.F. Froment, P.A. Jacobs, J. Catal. 174 (1998) 177.
[14] K.-C. Park, S.-K. Ihm, Appl. Catal. A 203 (2000) 201.
[15] M.C. Claude, J.A. Martens, J. Catal. 190 (2000) 39.
[16] M.C. Claude, G. Vanbutsele, J.A. Martens, J. Catal. 203 (2001) 213.
[17] J.A. Munoz Arroyo, G.G. Martens, G.F. Froment, G.B. Marin, P.A. Jacobs, J.A. Martens, Appl. Catal. 192 (2000) 9.
[18] R.A. Ocakoglu, J.F.M. Denayer, G.B. Marin, J.A. Martens, G.V. Baron, J. Phys. Chem. B 107 (2003) 398, DOI: 10.1021/jp0264533.
[19] J.F.M. Denayer, G.V. Baron, G. Vanbutsele, P.A. Jacobs, J.A. Martens, Chem. Eng. Sci. 54 (1999) 3553.
[20] L.M.Th. Maesen, M. Schenk, T.J.H. Vlugt, J.P. De Jonge, B. Smit, J. Catal. 188 (1999) 403.
[21] L.M.Th. Maesen, M. Schenk, T.J.H. Vlugt, J.P. De Jonge, B. Smit, J. Catal. 203 (2001) 281.
[22] M. Schenk, B. Smit, T.J.H. Vlugt, L.M.Th. Maesen, Angew. Chem. Int. Ed. 40 (2001) 736.
[23] P.B. Weisz, Adv. Catal. 13 (1962) 137.
[24] F.J.M.M. De Gauw, J. van Grondelle, R.A. van Santen, J. Catal. 204 (2001) 53.
[25] A.M. Myers, J.M. Prausnitz, AIChE J. 11 (1965) 121.
[26] R.T. Yang, Gas Separation by Adsorption Processes, Imperial College Press, London, 1997.
[27] E. Costa, J.L. Sotelo, G. Calleja, C. Marion, AIChE J. 27 (1981) 5.
[28] R. Krishna, Trans. IchemE 79 (A) (2001) 182.
[29] S. Ernst, J. Wietkamp, J.A. Martens, P.A. Jacobs, Appl. Catal. A 48 (1989) 137.
[30] D.M. Ruthven, Principles of Adsorption and Adsorption Processes, Wiley, New York, 1984.
[31] J.H. de Broer, S. Kruyer, Proc. K. Ned. Acad. Wet. 56 (1952) 451.
[32] G.F. Froment, L.H. Hosten, in: J.R. Anderson, M. Boudart (Eds.), in: Catalysis Science and Technology, Vol. 2, Springer, Berlin, 1981, p. 121, Chap. 3.
[33] G.E.P. Box, Ann. N.Y. Acad. Sci. 86 (1960) 792.
[34] N.R. Draper, H. Smith, Applied Regression Analysis, Wiley, New York, 1968, p. 284.
[35] H.O. Hartley, Technometrics 3 (1961) 269.
[36] W.E. Stewart, M. Caracotsios, J.P. Sorensen, AIChE J. 38 (1992) 641, 1302, Errata.
[37] G.E.P. Box, G.C. Tiao, Bayesian Inference in Statistical Analysis, Addison–Wesley, Reading, MA, 1973, reprinted by Wiley, New York, 1992.
[38] GregPak solver, Athena Visual Work Bench, version 8.2, Copyright: Stewart and Associates Engineering software Inc. http://www.athenavisual.com.
[39] F. Eder, J.A. Lercher, J. Phys Chem. B 101 (1997) 1273.
[40] G.G. Martens, G.B. Marin, J.A. Martens, P.A. Jacobs, G.V. Baron, J. Catal. 195 (2000) 253.
[41] H.C. Beirnaert, J.R. Alleman, G.B. Marin, Ind. Eng. Chem. Res. 40 (2001) 1337.