

Correlation between initial heats of adsorption and structural parameters of molecular sieves with different chemical composition — a calorimetric study

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Abstract - Calorimetric measurements of the differential molar adsorption heat of nonpolar molecules onto molecular sieves reveal that the initial adsorption heats

- increase linearly with the molar aluminium fraction of the adsorbents, which have the same crystal structure but different chemical composition and also
- increase with the framework density of the adsorbents, which have the same chemical composition but different crystal structure.

INTRODUCTION

Adsorption phenomena are of high scientific interest and widely used in practical application. Nevertheless, up to date it is not possible to calculate the adsorption equilibrium in advance due to the fact that it depends on many parameters (beside pressure and temperature on the crystal structure, the chemical composition, the nature and number of cations, et al.). Experimental investigations of the adsorption equilibrium are time-consuming and expensive. Therefore, attempts were made to minimize the necessary experimental effort. We showed that a reduced isotherm equation (ref. 1) describes a whole family of isotherms and that it is possible to calculate further isotherms knowing the initial heat of adsorption and one measured isotherm. The estimation of the zero adsorption heat is a necessary condition to apply the reduced isotherm equation.

Correlations between initial heats of adsorption and structural parameters of molecular sieves were already presented in (refs. 2, 3). The investigations confined to nonpolar molecules in order to include only dispersion interaction between the molecular sieves and the adsorbates. Two different series of molecular sieves were studied by using always the same adsorbates:

- zeolites with the same pore diameter (PD) but different Si/Al-ratios thus allowing to derive empirical relations $Q_0 = f(\text{Si/Al})_{\text{PD}}$ and
- molecular sieves with the same chemical composition but different pore diameters thus allowing to derive empirical relations $Q_0 = f(\text{PD})_{\text{Si/Al}}$.

n-Paraffins were preferentially used as adsorbates and in some cases cycloalkanes and benzene.

In this paper the results of the continuation of the mentioned studies are presented including not only aluminosilicates but also aluminophosphates.

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EXPERIMENTAL

The differential molar heats of adsorption were measured using a Calvet-type microcalorimeter (Setaram) at a temperature of 303 K. Adsorption isotherms were determined simultaneously at the same temperature using a standard volumetric adsorption apparatus which was connected to the calorimetric equipment. More experimental details are given in (ref. 4). The isosteric heats of adsorption were calculated from isosteric measurements. This method is described in (ref. 5).

Prior to both types of adsorption measurements, the adsorbents were activated in vacuum ($P < 1$ mPa) at 670 K for 24h. In the case of VPI-5 the adsorbent was evacuated (overnight) at room temperature before the activation started with a low increase of temperature up to 670 K (12h).

The AlPO_4 -5 (ref. 6) and AlPO_4 -11 (ref. 7) samples were synthesized following the procedure given by Flanigen and coworkers (ref. 8). VPI-5 was prepared according to a new way (ref. 9) and was characterized using different physico-chemical method (ref. 10). The silica faujasite (US-Ex) and silica mordenite were prepared by thermochemical dealumination methods (refs. 11, 12). Finally, the silica ZSM-5 (sili-calite) was synthesized according to (ref. 13). Some characteristic data of these molecular sieves are listed in Table 1.

TABLE 1. Characteristic data of the samples.

Sample	Framework density (FD) T/nm^3	Pore diameter (PD) nm	Pore volume cm^3/g	Oxygen-rings	Network dimensionality
US-Ex	13.57	1.16	0.300	12	III
MOR	17.15	0.7 x 0.65	0.20	12	I
MFI	18.00	0.53 x 0.56 0.51 x 0.55	0.19	10	III
MEL	17.78	0.53 x 0.54	0.16	10	III
AlPO_4 -11	19.1	0.63 x 0.39	0.073	10	I
AlPO_4 -5	17.32	0.73	0.120	12	I
VPI-5	14.2	1.21	0.183	18	I

RESULTS AND DISCUSSION

Though the measurements included both the n-paraffins up to n-hexane and benzene, the presented results concentrate initially on small molecules, especially on ethane. Figure 1 and 2 show the adsorption isosteres of ethane and n-hexane on the silica mordenite, respectively. The numbers at the isosteres indicate to the adsorbed amount (expressed in mmol/g). As illustrated in Fig. 2 the isosteres of n-hexane exhibit some deviations from the straight line (at a higher degree of adsorbed amount). For the calculations of the adsorption heat only the upper part of the n-hexane isosteres was used. (Reasons for curved isosteres are given in (refs. 14,15) and will not be discussed here). From Fig. 3 it is seen that the relationship between the differential molar heats of ethane on the three dealuminated mordenites and the adsorbed amount is linear. The dotted horizontal line is the heat of vaporization at 303 K. The initial heat of adsorption is determined by extrapolation of the straight lines to the ordinate axis. Obviously,

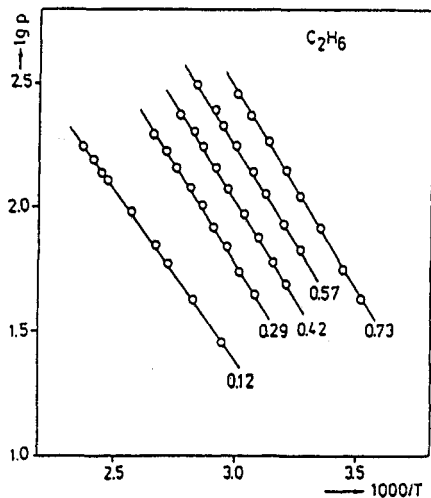


Fig. 1. Isosteres of ethane on H-mordenite.

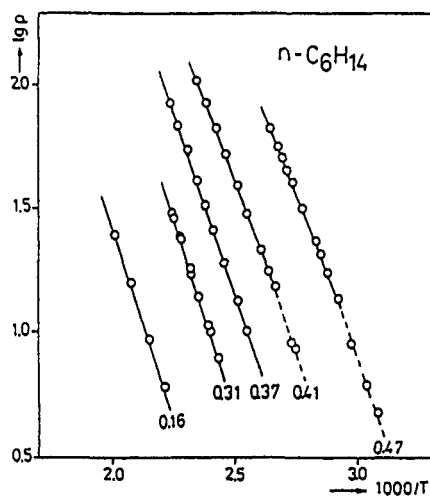


Fig. 2. Isosteres of n-hexane on H-mordenite.

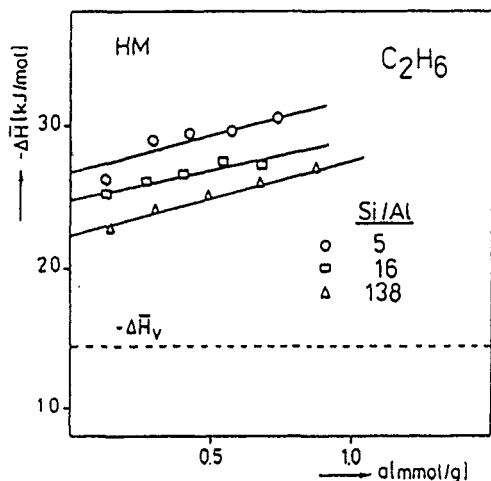


Fig. 3. Differential molar adsorption heats on H-mordenites.

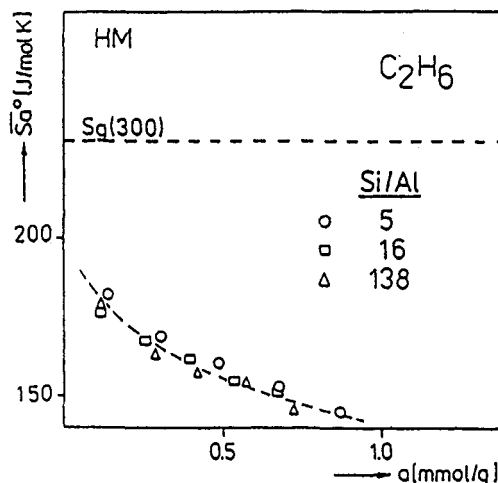


Fig. 4. Differential molar adsorption entropies on H-mordenites.

the adsorption heat of ethane on the different mordenites increases with decreasing Si/Al ratio, i.e. with increasing aluminium content of the framework.

As was previously shown for other systems, the differential molar adsorption entropies of ethane also do not depend on the electrostatic field of the mordenite pores (Fig. 4). Figures 3 and 4 illustrate that the heat of adsorption of nonpolar molecules on zeolites with the same pore diameter but different chemical composition is preferentially affected by the electrostatic potential of the adsorbent whereas the adsorption entropy is not affected.

In order to compare the initial adsorption heat of ethane on zeolites with different chemical composition and different pore diameter these values are plotted as a function of the molar aluminium ratio (m) of the molecular sieves investigated (Fig. 5). The following linear equations describe the influence of m on the zero adsorption heats:

$$\begin{aligned}
 Q_o &= 21.2 + 18.75 m && \text{FAU} && (1) \\
 Q_o &= 22.7 + 26.18 m && \text{MOR} && (2) \\
 Q_o &= 29.0 + 212.50 m && \text{MFI} && (3)
 \end{aligned}$$

At the same molar aluminium ratio the initial adsorption heats of ethane are changed exponentially with the decrease of the pore diameter of the adsorbents. This is in agreement with our results published some years ago concerning the adsorption of n-paraffins on silica faujasite, silicalite, aerosil and silicagels (ref. 2). We can derive from Fig. 5 that this relationship is not only valid for SiO₂-adsorbents but for aluminosilicates, too.

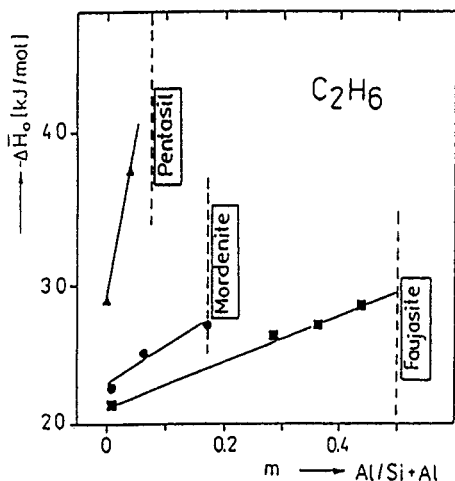


Fig. 5. Dependence of initial adsorption heats on the aluminium molar fraction.

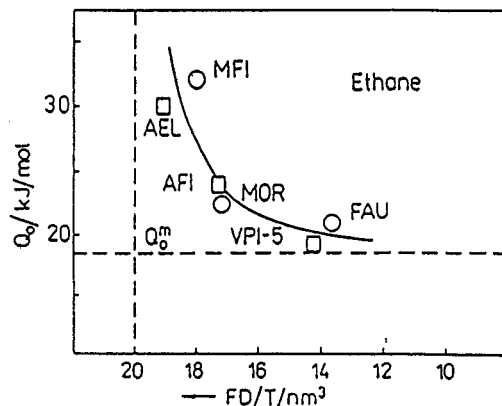


Fig. 6. Dependence of initial adsorption heats on the framework density (FD).

The data given in Table 1 demonstrate that the framework density (FD) changes inversely with the pore diameter of the aluminosilicates and -phosphates investigated. In the case of increasing FD-values higher initial heats of ethane can be expected. In fact, the values in Fig. 6 confirm this assumption. The correlations between the initial heats of ethane adsorption on the chemical composition and the framework density (or the pore diameter) exist for the other n-paraffins and further nonpolar molecules, too.

The following Fig. 7 presents the calorimetrically measured differential molar adsorption heats of ethane, n-butane, n-pentane and n-hexane on AlPO₄-11. The zero-coverage heat (Q_0) increases step by step with increasing number of CH₂-groups of the molecules (Table 2).

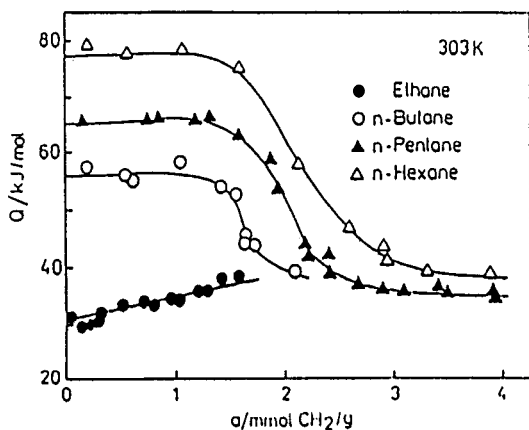


Fig. 7. Differential molar adsorption heats of n-paraffins on AlPO₄-11.

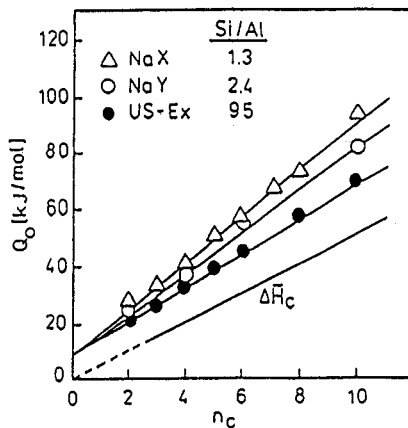


Fig. 8. Dependence of initial adsorption heats of n-paraffins on n_c .

TABLE 2. Initial heats of adsorption of nonpolar molecules on molecular sieves investigated.

Sample	C ₂ H ₆	n-C ₄ H ₁₀	n-C ₅ H ₁₂ kJ/mol	n-C ₆ H ₁₄	C ₆ H ₆
VPI-5	19.0	28.0	35.0	42.5	40.0
AFI	23.9	40.6	49.0	59.0	54.4
AEL	33.0	53.0	64.0	74.5	58.5
FAU	20.9	34.3	41.0	47.3	45.0
MFI	29.0	51.0	63.5	70.3	57.8

TABLE 3. Incremental values of adsorption heats for CH₃- and CH₂- groups of n-paraffins.

Sample	Q _o ^{CH₃} kJ/mol	Q _o ^{CH₂} kJ/mol
VPI-5	9.50	5.81
AFI	11.95	8.69
AEL	16.50	10.79
FAU	10.45	8.09
MOR	11.25	9.12
MFI	16.0	9.81

Using the initial adsorption heats (of Table 2) it is possible to derive increment values for the n-paraffins adsorbed on the different molecular sieves. These data are listed in the columns 2 and 3 of Table 3. It is important to note that all molecular sieves presented are electrical neutral, i.e. the zeolites are dealuminated to a high degree thus possessing large Si/Al ratio. Applying the given values a calculation of the initial heats of adsorption is possible for all n-paraffins (at least up to n-decane) on the studied molecular sieves. This implies that the correlation between the initial heats of adsorption and the C-numbers of the n-paraffins is linear. For the zeolites and the aluminophosphates Figs. 8 and 9 show that this assumption is correct. As may be seen from the figures the zero adsorption heats are

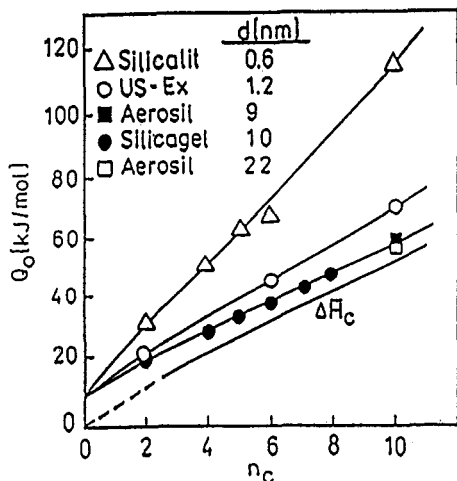


Fig. 9. Dependence of initial adsorption heats on n_c.

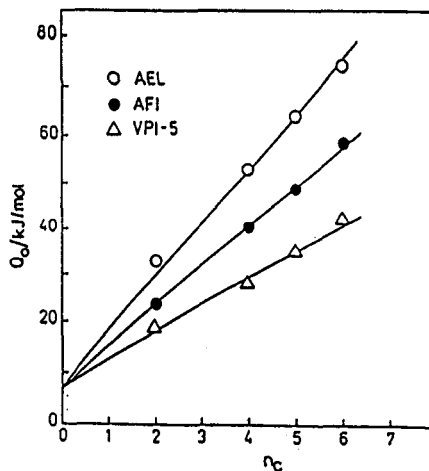


Fig. 10. Dependence of initial adsorption heats on n_c.

described by straight lines intersecting at the same value on the ordinate axis. The corresponding equations are:

$$\begin{aligned}
 Q_o &= 8.0 + 8.4 n_c & \text{NaX} & \quad (4) & Q_o &= 8.0 + 10.4 n_c & \text{Silicalite} & \quad (7) \\
 Q_o &= 8.0 + 7.3 n_c & \text{NaY} & \quad (5) & Q_o &= 8.0 + 4.7 n_c & \text{Silicagel} & \quad (8) \\
 Q_o &= 8.0 + 6.0 n_c & \text{Us-Ex} & \quad (6) & & & & \quad (\text{some data are given in (ref. 16)})
 \end{aligned}$$

Recently Derouane et al. (refs. 17,18,19) derived a simple equation to calculate the initial adsorption heat in advance:

$$Q_o = RT + C_m \cdot C_2 \cdot W_r(s) \tag{9}$$

where C_m - constant, depends only on the physical properties of the adsorbate ($C_m = (\alpha/d^3)$); C_2 - constant, depends only on the properties of the molecular sieve and has been estimated by an iteration procedure using experimentally determined zero adsorption heats of noble gases; $Wr(s)$ - represents the extrinsic effect of geometrical surface curvature, depends on the diameter of the adsorbate and adsorbent. Derouane claimed (ref. 18) that the equation is valid for the physical adsorption of small nonpolar molecules and that the constant C_2 is 112.75 for all aluminosilicates and 98.9 for all (silico)-aluminophosphates. He states furthermore that the chemical composition is of minor influence, meaning that the results change only by a factor of about 0.1 (ref. 20). Equation 9 is interesting because it demonstrates evidently the dominant influence of the ratio of the critical adsorbate diameter and the pore diameter on the adsorption heat. We tested the validity of these equation by using our experimental data of small nonpolar molecules. Some results are presented in Tables 4 and 5.

TABLE 4. Comparison between experimental and calculated initial adsorption heats of nonpolar molecules on different zeolites.

Zeolite	molecule	$Q_0^{exp.}$	$Q_0^{calc.}$
		kJ/mol	
NaX	Ethane	28.5	22.8
US-Ex	Ethane	21.3	22.8
Na-ZSM-5	Ethane	37.5	30.5
H-MOR	Ethane	27.0	34.6
NaY	Xenon	16.3	23.7
Na-ZSM-5	Xenon	27.8	30.8

TABLE 5. Comparison between C_2 data given in (ref. 20) and calculated values using equations presented therein.

Zeolite	molecule	$C_2^{calc.}$	C_2^a
NaX	Ethane	144.6	112.75
US-Ex	Ethane	105.1	112.75
Na-ZSM-5	Ethane	140.9	112.75
H-MOR	Ethane	85.9	112.75
NaY	Xenon	73.3	112.75
Na-ZSM-5	Xenon	100.7	112.75

a: given in (ref. 20)

From the tables the following conclusions can be drawn:

- C_2 is not a constant whether for all aluminosilicates nor for all aluminophosphates. (The data for the aluminophosphates are not given here).
- C_2 depends on the chemical composition of the zeolites to a stronger extent than stated by Derouane (ref. 20).

Nevertheless, for different molecules on the same type of molecular sieves the equation 10 seems to be useful.

About twenty years ago it was shown (in ref. 21) that between the dispersion interaction of one isolated gas molecule with an adsorbent and the critical parameters of the gas (T_c , p_c) exists a very simple correlation:

$$-\Delta\bar{U}_0 = D T_c/p_c^{1/2} \quad (10)$$

where $-\Delta\bar{U}_0$ - adsorption energy for a $\rightarrow 0$ and D - proportionality factor. Furthermore it was demonstrated in the same paper that the equation 10 is valid in the case of adsorption of gases and vapours on the energetical homogeneous graphitized thermal soot (GTS). Due to the fact that the zeolites are in comparison to GTS more complex with regard to the geometrical and chemical properties it was expected that the presented equation should be valid especially for the energetical homogeneous zeolites, i.e. for samples without an electrostatic field in the pores and cavities. That was indeed what we found for the ad-

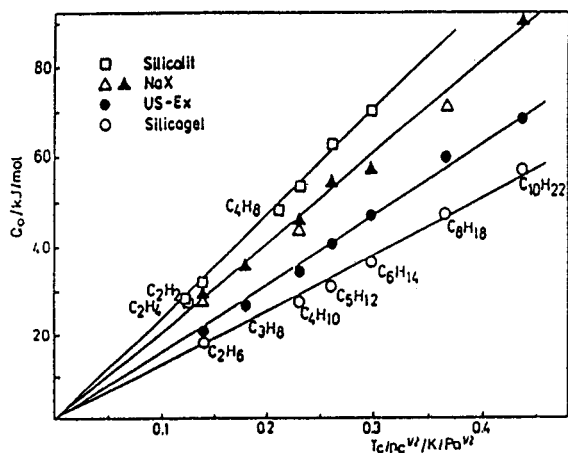


Fig. 11. Dependence of initial adsorption heats on critical parameters.

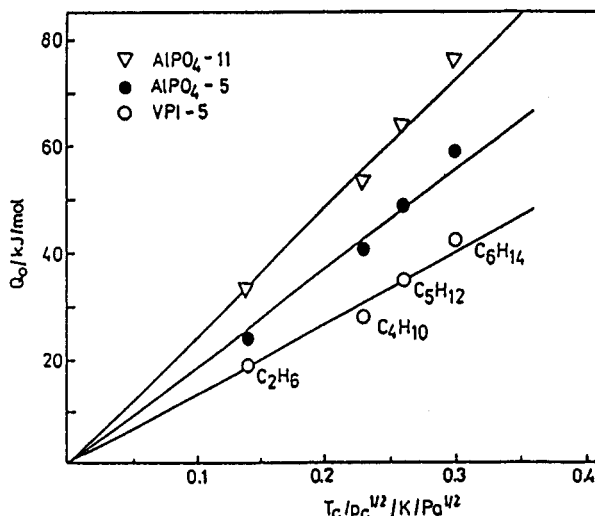


Fig. 12. Dependence of initial adsorption heats on critical parameters.

sorption of nonspecific and specific adsorbates (ref. 22) on silicalite and only nonspecific molecules on a dealuminated Y-zeolite (ref. 22). The difference in the behaviour between both microporous SiO_2 -adsorbents was explained by the relative large amount of aluminium in the framework of US-Ex and a corresponding number of Brönsted sites acting as center of adsorption and reaction for specific molecules.

The aluminophosphates should behave similarly like silicalite concerning the energetical homogeneity of the pore systems. It seemed therefore to be of interest to examine whether equation 10 describes the dependence of the initial adsorption heat of nonpolar molecules in the aluminophosphates on their critical parameters, too. In Fig. 12 the zero adsorption heats of the n-paraffins on the three aluminophosphate samples are shown. As illustrated the zero heats of adsorption depend linearly on the critical parameters.

Figure 11 shows that the initial adsorption heats of the n-paraffins can be described by equation 10 in the case of the cationated NaX as well as in the case of silicagel. Therefore, it can be concluded that the evaluation of the zero adsorption heats of nonpolar molecules (at least of n-paraffins) is simple if the proportionality factor is known.

TABLE 6 D values of the systems studied.

Sample	D (kJ/mol)	FD (T/nm^3)	Sample	D (kJ/mol)	FD (T/nm^3)
NaX	202	12.7	AlPO_4 -11	241	19.1
US-Ex	157	13.6	AlPO_4 -5	185	17.3
MFI	236	18.0	VPI-5	134	14.2
Silicagel	127	-			

Table 6 lists D values for the n-paraffin adsorption on the adsorbents studied. Comparing the D number with the framework density it is seen that the proportionality factors increase with the compactness of the crystal structure. If the D values are plotted against the FD values the corresponding points do not arrange around one straight line but along two lines with the same slope. Molecular sieves with a

onedimensional network of pores can be described by one curve and molecular sieves with a threedimensional network by the second one. It can therefore be concluded that the D values are determined by the type of the pore network beside the framework density (or the reciprocal pore diameter).

The calorimetric measurements of the adsorption heats of nonpolar molecules on aluminosilicates and -phosphates allow the following conclusions:

The initial adsorption heats of n-paraffins increase linearly with the molar aluminium fraction of the given zeolite type. The slopes of the straight lines depend on the framework density of the molecular sieves. For neutral adsorbents (SiO_2 or AlPO_4) the initial adsorption heats of nonpolar molecules increase with increasing density of the T-atoms. The heats arrange around one curve independent on the molecular sieve type. The examination of two equations given in the literature shows that in both cases experimental values are necessary to calculate the initial heats of adsorption of nonpolar molecules in advance.

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