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A New Method for the Determination of Low Coverage Adsorption Heats for Zeolite-VOC Systems

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Abstract. In this paper, we present a new experimental technique and a mathematical procedure for the calculation of the isosteric heats of adsorption of VOC-zeolite systems. This procedure provides a continuous isosteric heat curve over a large coverage ratio range including the low-coverage area. Results are given for a toluene-NaY system at 423 K. The validity of the method is discussed by comparison with other methods.

Keywords: adsorption, dynamic flowing method, isosteric heat of adsorption, low coverage ratios

1. Introduction

The fundamental understanding of the adsorption of VOC compounds in the porous structure of zeolite adsorbents is of prime importance for the design of tailor-made adsorbents in the field of purification of VOC-loaded waste gases by adsorption process. For this purpose, the isosteric heat of adsorption extrapolated to the limit of zero coverage is interesting as it governs the dependence of the Henry constant with the temperature. It is also directly related to the interactions between the adsorbed molecules and the atoms of the zeolitic structure. The magnitude of the isosteric heat of adsorption is depending both on the atomic composition and molecular structure of the adsorbate molecules and on the atomic composition and topology of the adsorbent. Molecular-structure factors such as the polarity of the adsorbate molecules and the inclusion of non-framework ions have also a non negligible influence (Dunne et al., 1997).

The isosteric heats of adsorption can be determined using the isosteric method already presented elsewhere (Rouquerol et al., 1999). A determination based on the treatment of mass data obtained by the chromatographic method is also possible (Denayer et al., 1997). The fundamental assumption of this method is to describe the adsorption equilibrium by the Henry law. The coupling of static volumetry to calorimetry was also reported (Bellat et al., 2002). The purpose of this work is to present a new experimental technique and a mathematical treatment allowing the determination of a continuous isosteric heat curve over a large coverage ratio range. The experimental device is described, as well as the main steps of the experimental procedure. We also present a description of the mathematical procedure. Finally, the interest and the validity of the method are checked by studying the adsorption of toluene on a NaY zeolite at 423 K.

2. Apparatus and Procedure

The experimental apparatus (Fig. 1) is already described elsewhere (Dutour et al., 2004). The main component is a thermoanalyzer (model TG-DSC 111 provided by Setaram, France) where a thermobalance [B111] is coupled to a Tian-Calvet calorimeter [DSC111] to allow the simultaneous measurement of mass (TG signal) and calorimetric (HF signal) adsorption data. A dynamic flowing technique is used, in which the adsorbent is kept under a constant carrier gas (helium) flow rate containing traces of a volatile organic compound. The temperature of the sample (T signal), regulated by a water-cooled electrical furnace, is also

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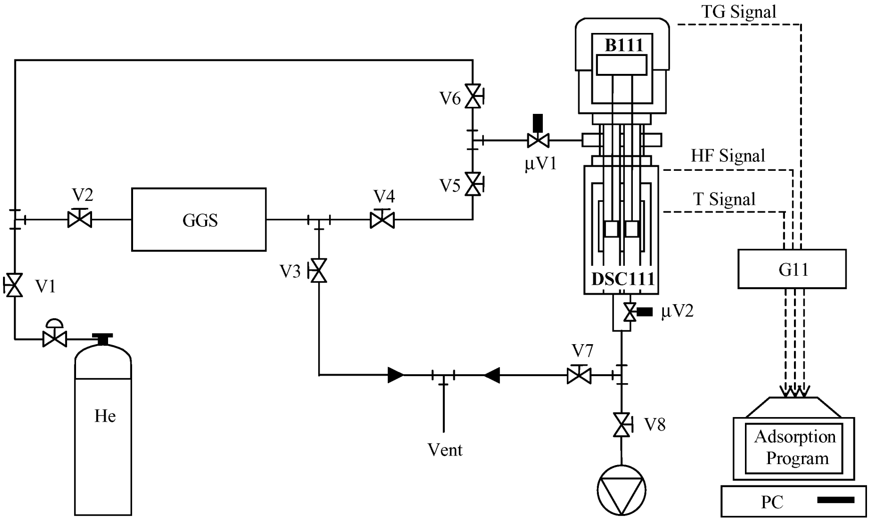

Figure 1. Experimental apparatus.

measured. The computer [PC] and controller [G11] perform the amplification, acquisition, digitalization and visualization of the TG, HF and T signals. They also control and program the temperature of the calorimeter. The external circuit is made of tubes, valves [V1–V8] and microvalves [μV1 and μV2]. It also comprises a gas generation system [GGS] producing VOC-helium mixtures by two different techniques. The first one (technique A) consists in saturating the helium flow by bubbling it through the liquid VOC contained in a saturator maintained at constant temperature. The VOC molar ratio of the mixture generally ranges from a few hundred up to a few thousand ppm depending on both the vapour pressure law of the organic compound and the temperature limits of the thermostated bath. In the case of technique B, the vapours emitted by a porous tube filled with liquid VOC and kept within an oven at constant temperature and pressure are diluted in helium to achieve the required mixture. This system was purchased from Calibrage (France) and completes technique A as it covers the low VOC molar ratio range (approximately from 1 to 1000 ppm).

The experimental procedure is rather complex. It is presented here quite briefly but a detailed description is given in a previous paper (Dutour et al., 2004). Prior to each adsorption experiment, the zeolite sample is outgassed overnight at 673 K under dynamic vacuum. It is then cooled down and maintained two hours at the adsorption temperature for complete thermal homogenisation. Those two last steps are performed under helium flowing to avoid any parasitical air adsorption onto the clean adsorbent sample. The adsorption run is started by switching from the pure helium flow to the VOC-helium mixture. The equilibrium state is characterized by the constancy in the time of both the TG and HF signals. Figure 2 shows an example of the mass and calorimetric signals recorded during a typical adsorption experiment.

3. Theoretical Treatment of the Signals

This section aims at presenting a new method for the determination of the isosteric heat of adsorption on the basis of the TG and HF signals resulting from the adsorption on a zeolite adsorbent of a pure VOC in a helium flow. This method provides a continuous isosteric heat curve as a function of the adsorbent coverage ratio and rests on the assumption that the TG and HF signals are time-consistent.

3.1. Expression of the Isosteric Heat of Adsorption

It can be established that the HF signal and the isosteric heat of adsorption (Δh_{st}) are related by:

$$\Delta h_{\mathrm{st}} = -\frac{\mathrm{HF}_{\mathrm{inst}}(t)}{q_{\mathrm{VOC-ads}}}(t) \tag{1}$$

in which $q_{\mathrm{VOC-ads}}(t)$ is the adsorption mass flow rate (g s^{-1}) and $\mathrm{HF}_{\mathrm{inst}}(t)$ is the heat flow rate (*W*). Both $\mathrm{HF}_{\mathrm{inst}}$

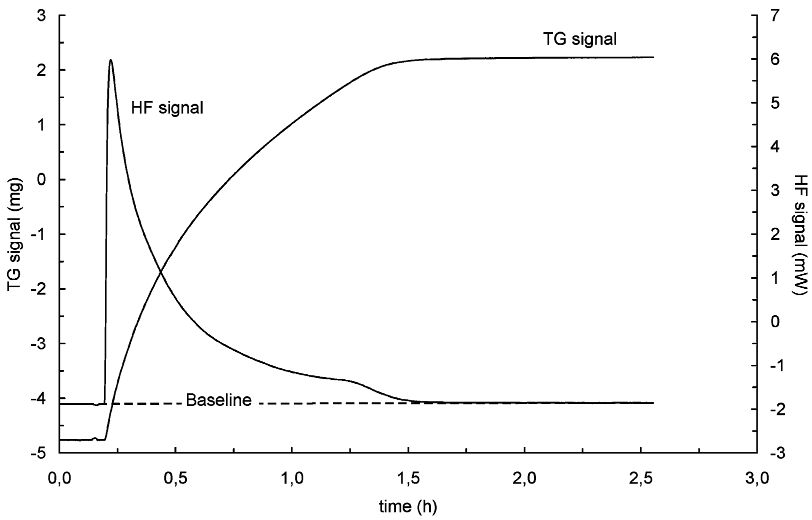

Figure 2. Example of experimental TG and HF signals.

and $q_{\text{VOC-ads}}$ are taken for a given time *t*. The adsorption mass flow rate vs. time curve ($q_{\text{VOC-ads}}$ signal) is simply given by the derivative of the TG signal with respect to the time *t*:

$$q_{\text{VOC-ads}}(t) = \frac{d\text{TG}(t)}{dt} \tag{2}$$

The TG vs. time signal resulting from an adsorption experiment is smoothed by a sixth-order polynomial using the least squares method so that the derivative can be calculated easily. The heat flow rate HF_{inst} can be obtained from the HF signal by:

$$\text{HF}_{\text{inst}}(t) = \text{HF}(t) + \tau \cdot \frac{d\text{HF}(t)}{dt} \tag{3}$$

in which τ is the response time of the calorimeter. The response time of the calorimeter is mainly dependent on the design of the apparatus, the type of the crucibles (plain or latticed walls) and the mass of the sample. It is also slightly influenced by the experimental temperature. One can determine τ assuming that the calorimeter response to a thermal pulse (instantaneous perturbation) should be a HF peak with a quasi infinite initial slope followed by an exponential return to the baseline. We induced this thermal pulse by suddenly heating the adsorbent from the ambient temperature (the crucibles are outside the calorimeter) to the experimental temperature (the crucibles are descended inside the calorimeter). The rough signal detected by the heat-flux transducers at 423 K (Fig. 3) is too flat to give an accurate picture of the thermal effect under study. As a result, we corrected it using Eq. (3) with different response times. At 423 K, the real response time of the calorimeter is $\tau = 29$ s. This value gives indeed an optimal exponential return to the baseline: for $\tau = 28$ s, it is too slow (existence of a drag) whereas the bump presented by the $\tau = 30$ s curve has no physical meaning.

Prior to the determination of the calorimeter response time, the experimental HF vs. time signal is smoothed by a cubic spline. Basically, this method consists in approximating the calorimetric peak by a series of polynomials (order ≤ 3) constructed in $[t_{i-1}, t_i[$ intervals ($i = 1, \ldots n$) determined by the time abscissas. Equations (1), (2) and (3) applied for each instant *t* of the experimental run lead to the determination of $\Delta h_{\text{st}} = f(t)$. The evolution of the coverage ratio as a function of *t* is determined by dividing each point of the TG signal by the outgassed sample mass m_{os}:

$$\theta(t) = \frac{\text{TG}(t)}{m_{\text{os}}} \tag{4}$$

The procedure for the determination of the outgassed sample mass is already presented elsewhere (Dutour et al., 2004). Combining $\Delta h_{\text{st}}(t)$ and $\theta(t)$, it is possible to obtain $\Delta h_{\text{st}} = f(\theta)$. The maximal θ value is obtained at the adsorption equilibrium (θ_{eq}). It is dependent on the molar ratio of the VOC-helium mixture

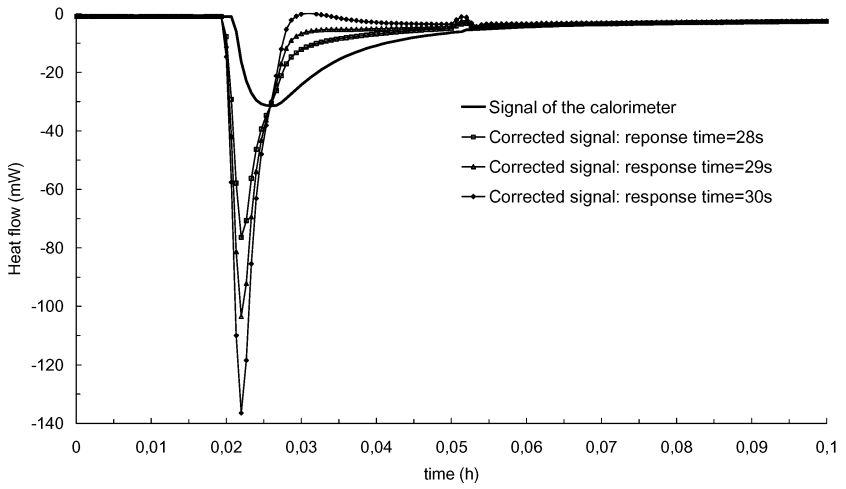

Figure 3. Determination of the response time of the calorimeter.

under study as this one fixes the VOC partial pressure of the gaseous phase surrounding the adsorbent sample. As a result, one set of experimental TG and HF signals only provides the part of the global isosteric heat vs. coverage ratio curve ranging from $\theta = 0$ to θ_{eq} (this part of the Δh_{st} curve is referred to below as a 'pseudo-isosteric heat of adsorption curve').

4. Experimental Section

The experimental results presented in this paper were obtained from the study of a toluene-NaY system at 423 K. The zeolite (Si/Al 2.43) was provided by the Institut Français du Pétrole (IFP, France). The toluene was purchased from Aldrich with a purity of 99.8%. Our method was validated in the low coverage area of the isosteric heat vs. coverage ratio curve by studying the adsorption of toluene-helium mixtures with different molar ratios. Those mixtures (42, 59, 84 and 105 ppm toluene in helium) were generated using technique B.

4.1. Pseudo-Isosteric Heat of Adsorption Curves

Figure 4 shows the pseudo-isosteric heat of adsorption curves derived from the experimental TG and HF

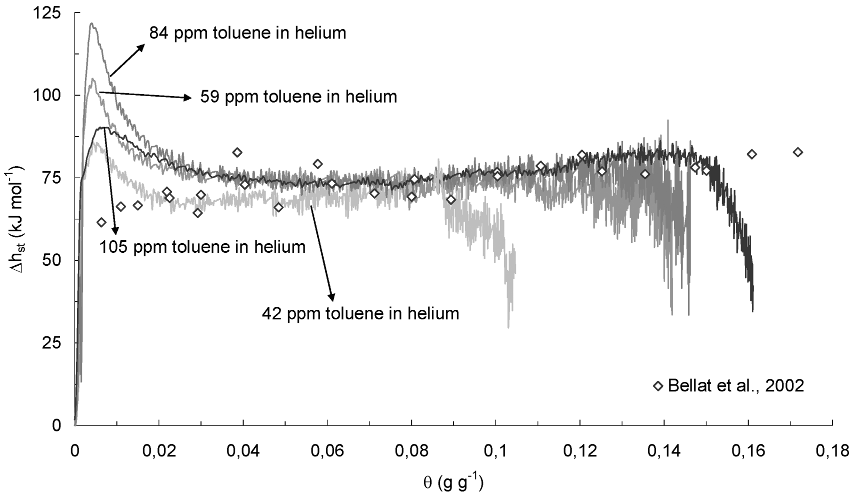

Figure 4. Isosteric heats of adsorption in the low coverage range (study of the toluene-NaY system at 423 K).

signals. The maximal coverage ratio of each curve is dependent on the molar ratio of the mixture: this one fixes indeed the total quantity of toluene adsorbed by the sample. The curves overlap one another over a quite extended coverage ratio range (approximately from $\theta = 0.02$ to 0.12 g g^{-1}) with a dispersion of about 10 kJ mole^{-1}. As shown by Fig. 4, the isosteric heats calculated with our method (mean value: -72.7 kJ mol^{-1}) are consistent with discontinuous values (mean value: -72.6 kJ mol^{-1}) obtained for the same toluene-NaY system by Bellat et al. using a volumetric apparatus coupled to a calorimeter. Our results are also comparable to the isosteric heat value (-70.3 kJ mol^{-1}) determined by a chromatographic technique (Nokerman et al., 2004). The peaks observed for $\theta \leq 0.02$ g g^{-1} are characteristic of the limitations of our method. When the adsorption phenomenon is very rapid (it is typically the case at the beginning of an adsorption run), the slope of the experimental HF signal is very sharp. Therefore, a small inaccuracy in the determination of the response time of the calorimeter is sufficient to induce an important error on the HF_{inst} signal and thus on the determination of the isosteric heats of adsorption. We also see from Fig. 4 that the end part of the pseudo-isosteric heat curves is always noisier. This is explained by the fact that near the adsorption equilibrium, both the numerator and the denominator of Eq. (1) are close to zero (mathematical limitation).

4.2. *Conclusion*

We have developed a new method for the determination of the isosteric heats of adsorption of VOC-zeolite systems. This method provides a continuous isosteric heat vs. coverage ratio curve and is based on the treatment of the mass and calorimetric signals provided by a thermobalance coupled to a calorimeter (dynamic flowing technique). The entire isosteric heat curve can be constructed provided a small number of experimental runs are performed. As to cover a large coverage ratio range, these experiments must be relative to the adsorption of VOC-helium mixtures with very different molar ratios. Our method was validated by studying the adsorption of toluene on a NaY zeolite and comparing the results with the one obtained by other techniques (the coupling of a volumetric apparatus to a calorimeter and the chromatographic method). All the methods appear to be globally coherent. Our method however fails in the prediction of the very low coverage ratio heats of adsorption ($\theta < 0.02$ g g^{-1}) as a result of the important adsorption rates characterizing the first minutes of the adsorption runs.

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