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Design parameters for the construction and operation of heat-flow calorimeters

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Abstract

Several important design parameters for the construction and operation of a Tian–Calvet heat-flow calorimeter used in the study of adsorption and catalysis are presented. Both heat transfer and adsorption dynamics must be considered in the design. Improper choice of length scales for adsorption and heat transfer, and of the temperature used in making the measurements, can result in serious errors. A general methodology for ensuring that adsorption equilibrium is achieved is discussed. © 1998 Elsevier Science B.V.

Keywords: Tian–Calvet heat-flow calorimeter; Adsorption; Catalysis

1. Introduction

Calorimetry is one of the standard, text-book techniques for measuring the thermochemistry of a wide range of chemical processes. It has also been applied to the study of adsorption and catalysis; however, due to the nontrivial nature of the measurements, calorimetry has remained the specialty of a relatively small number of research groups in these subfields. Even so, there is extensive literature on the subject and much has been learned about adsorption from calorimetric measurements. Several excellent reviews have been written, to which we refer the interested reader [1–3].

A number of papers have also been written describing the design of microcalorimeters for adsorption measurements. We refer the reader to several here, although there are a number of other designs [2–5]. With the advent of low-cost, high-sensitivity, heat-flux sensors and inexpensive computer data-acquisition systems, it is relatively easy to build one; and a number of the published designs appear to be satisfactory. However, we have found that, during the construction of our own instrument, it was necessary to reinvent several key design considerations [6]. While microcalorimeters are conceptually simple devices, there are subtle issues associated with heat losses and the time needed for reaching equilibrium. If these factors are not properly considered, the measurements will be erroneous and the results inconsistent. In this paper, we will examine those design issues which we found most important for building a "home-made" microcalorimeter for adsorption measurements. We will discuss the critical parameters which need to be controlled in the design of the instrument. Finally, we will discuss the consistency checks which should be performed to ensure that the measurements are meaningful.

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2. Design parameters for heat-flow calorimeters: *General considerations*

We will restrict our consideration to heat-flow, or Tian–Calvet, calorimeters as applied to adsorption problems. A schematic diagram, which includes all of the basic features, is shown in Fig. 1. The heart of the calorimeter consists of the heat sink and the sample cell, separated by the thermopile, heat-flux sensors. Heat generated by the adsorption process slightly raises the sample temperature. The energy then flows through the sensor to the sink and the flux is measured as a function of time. Integration of the flux leads to the total heat collected. Usually, the signal from a reference cell is measured in series with the signal from the sample cell, so that baseline shifts and signal drift can be eliminated. The rest of the calorimeter consists of a temperature bath to fix the temperature of the sample and heat sink, a gas-handling system for dosing adsorbate onto the sample, and a data-collection system. Because we have found that a personal computer with an A/D board, capable of thermocouple inputs, is sufficient for data collection, we will not discuss this part of the system further. Before focusing on the details of heat transfer and adsorbate equilibrium rates in the sample cell, there are a few practical design considerations which we have found helpful, even though they appear obvious in retrospect. First, many molecules of interest, such as ammonia and water, tend to adsorb on the wall of the adsorbate loop and gas-handling system. Adsorption on the walls can lead to serious errors, particularly in the initial data points taken at low coverages, because the dose admitted to the sample is not accurately known. This problem can be easily avoided by heating the adsorbate loop and all tubing leading to the sample cell. While this can be accomplished with heating tape, we believe there are advantages in making the temperature bath sufficiently large so as to include all of the components which could potentially adsorb or release adsorbate, as shown in Fig. 1. Because most pressure manometers cannot be heated, it may be necessary to measure the pressure in the adsorbate loop indirectly, before and after equilibrating it with the sample [6], as we have discussed elsewhere.

Second, the size of the heat sink should be chosen so that the time constant associated with temperature changes in the bath are long in comparison with the measurements. For example, if the heat sink is heated by free convection in the temperature bath, temperature fluctuations in the sink will be described by:

$$\{mC_{\mathrm{p}}\}\mathrm{d}T/\mathrm{d}t = hA(T - T_0)$$

where T and T_0 are, respectively, the temperatures of the sink and the bath, m the mass of the block, C_{p} the heat capacity, h the heat-transfer coefficient, and A the external area of the heat sink. (More generally, the

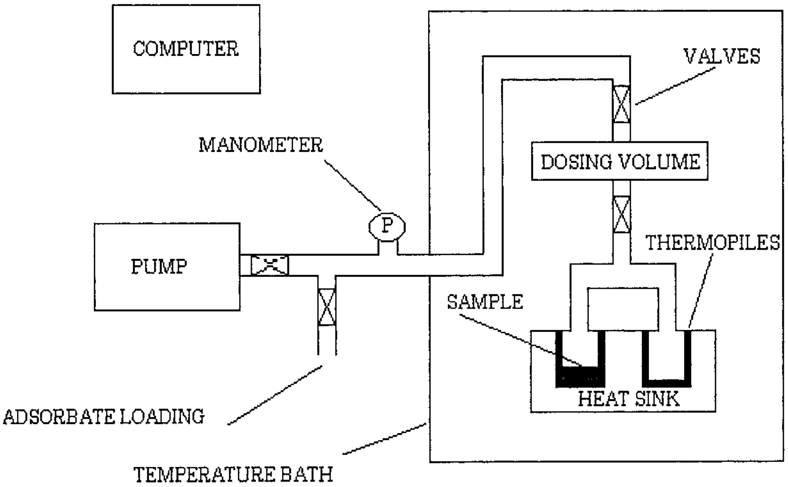

Fig. 1. Basic diagram of a Tian–Calvet type calorimeter, similar to that used (Ref. [6]).

right-hand side of this equation will depend on the manner in which the temperature of the sink is controlled.) The foregoing equation leads to a time constant of $\{mC_p/hA\}$ for temperature changes in the sink and this should be long compared to the time necessary to collect all of the heat from a dose of adsorbate. Assuming that one must collect heat-flux data for $\sim$15 min, and that one should have a time constant for fluctuation in the sink that is $\sim$10 times this value, typical numbers for h lead to the conclusion that one must have a sink with a mass that is at least several kilograms.

One obviously desires to relate the heats that are measured calorimetrically to thermodynamic properties, usually Δu, the differential energy (or heat) of adsorption, or Δh, the isosteric heat of adsorption [1]; but the heat registered by the calorimeter depends on the design of the instrument. For example, if a gas dose enters the calorimeter at the temperature of the sample cell and an equal number of moles enter a reference cell, it is has been shown that the calorimetric heat is the isosteric heat [1]. In some applications, where volume is to be minimized, no reference cell is employed [7,8]. If the adsorbate dose is then admitted to the sample cell through a capillary tube so that the expanding gas remains isothermal and the energy associated with expansion is not collected by the calorimeter, the calorimetric heat is the differential heat [1,7]. However, since it may not be easy to obtain a truly isothermal expansion, the energy associated with the expansion should be measured. Because work terms associated with admitting adsorbate into the sample cell are of the same order of magnitude as RT, they are sometimes negligible compared with the adsorption energy; but this may not be the case for every weak adsorption [9].

3. Design considerations for the sample cell

More critical to the operation of the microcalorimeter is the design of the sample cell and the conditions used for making the measurements. While one obviously seeks to minimize heat losses associated with an adsorption event, it is equally important to collect the heat as rapidly as possible, since this increases the signal from the thermopiles and minimizes the losses. Adsorption equilibrium must also be rapid in comparison with the time needed for measuring the heat associated with an adsorbate dose.

The geometry of the sample cell is obviously very important for each of the above considerations. The most commonly used geometry in calorimeter design is the cylinder with radial heat flow. While this geometry is simple and minimizes heat losses since only heat flowing in the axial direction is uncollected, adsorption must occur down a packed bed so that adsorption equilibration may be slow. Modifications to this basic design have been proposed in which a porous cylinder is placed in the middle of the sample cylinder, leaving the sample in the annular region between the thermopiles on the outside and the porous cylinder on the inside [10]. Adsorption can then occur radially into the sample, so that diffusion paths are short. Planar cells have also been built in which the sample is placed between two flat plates, with thermopiles on either side [11].

Finally, the design that we have used in our system, shown in Fig. 1, is a simple cube in which the sample is spread evenly over the bottom of the cube. The bed is maintained to be relatively thin and most of the heat is collected through the bottom thermopile, with the thermopiles on the sides collecting the residual heat that would otherwise flow up the wall of the cell. In this case, heat and mass transfer occur over the same critical length scales, making design for the application of interest less cumbersome. One of the nice features of the cubic design is that inexpensive, planar thermopiles can be purchased from in-stock items and modifications can be made easily. One concern with this design is that heat can be lost through the top, either through the gas phase or by radiation. While an additional thermopile with an opening to admit gases can probably be added, at the cost of some loss in flexibility and an increase in cell complexity, we have found that placing a thin layer of quartz chips above the sample bed leads to a slight increase in the amount of heat collected for each pulse ($\sim$5%) and is probably sufficient to account for losses from the top.

4. Adsorption dynamics

In general, equilibrium can only be assumed if the process is reversible in the time scale of the measurement. Conditions for which this is true are often difficult to achieve in typical calorimetric measurements of adsorption, so that one must proceed with caution. Usually, the sample is exposed to a series of adsorbate pulses and it is assumed that these titrate sites of decreasing energy. This is not generally true since adsorption equilibration may not be achieved. Even at equilibrium, the sites may not fill sequentially. We will come back to the equilibrium situation later in this section in order to focus, primarily, on equilibration rates due to migration in the bed.

From the foregoing considerations, we will assume that intrinsic adsorption rates, defined as a sticking coefficient times the surface flux, are always fast. While this may not always be true, there are no guarantees that adsorption rates will correlate with site energetics, so that other rate processes, including diffusion and desorption of molecules, will still define the equilibration rates. With this assumption, rates of adsorption equilibration are really determined by the time constants associated with adsorbed species at one point in the sample moving to other points in the sample bed. This obviously requires that the rate of desorption must be relatively fast.

The effect of intrinsic desorption rates ($r_{\mathrm{d,intr}}$), in the absence of transport processes, has already been considered in detail by others [1,12], with the conclusion that molecules with adsorption energies greater than ~200 kJ/mol are immobile, even for adsorption at 500 K. In porous adsorbents, however, observed desorption rates are not equal to the intrinsic rates due to coupling with transport processes. Observed rates are usually much lower than the intrinsic rates, by factors of 10^6 and larger [3,14]. Therefore, it is important to consider these issues of mobility and adsorption equilibration further.

5. Lessons from TPD

One of the best experimental methods for examining macroscopic mobility of adsorbates on porous solids is by temperature programmed desorption (TPD). For example, Fig. 2 shows TPD–TGA curves for pyridine on an H-ZSM-5 zeolite, using a very small sample (~15 mg) and desorption into a high vacuum (~10^{-7} torr) [15]. H-ZSM-5 is an acidic zeolite which contains one acid site for each Al atom in the structure. In the measurements from Fig. 2, the sample was initially saturated with pyridine, then evacuated for 1 h at room temperature to remove some of the weakly held species. For our present considerations, two important points can be taken from the results.

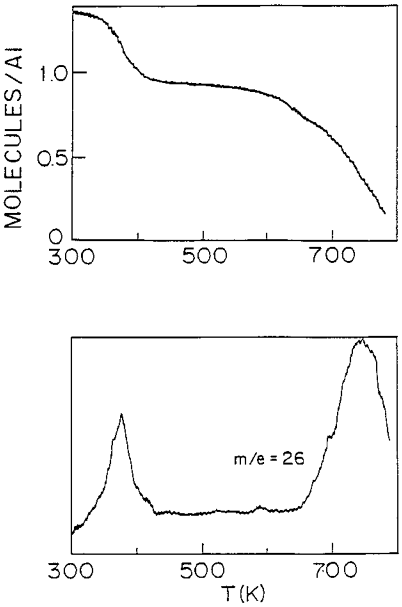

Fig. 2. TPD–TGA of pyridine on H-ZSM-5. The simultaneous measurements were carried out in high vacuum, using a mass spectrometer to measure the partial pressure (*m*/*e*=26) and a microbalance to monitor the sample mass. H-ZSM-5 is known to have one, strong Brønsted-acid site per framework Al. The figure is reproduced from Ref. [15].

First, even for desorption from very small samples, spread loosely on the bottom of a flat sample pan in high vacuum, weakly held species, in excess of one per site, cannot be removed in the 1 h time scale. The implication for adsorption of pulses into a much larger bed of H-ZSM-5, which may even have been pelletized, is that high temperatures are needed in order to probe the strong acid sites [4]. If molecules in a pulse adsorb at the front of the bed, or in the crystallites at the edge of the pellets, they will not be able to migrate to the strong acid sites, so that the measured heats will be that for adsorption at a mixture of different sites. Adsorption must be carried out at a minimum temperature of 400 K in order to avoid sampling some of the very weak sites in the initial pulses. Surface diffusion may assist equilibration within a given crystallite but is unlikely to ensure migration between pellets in a bed of zeolite, or even between crystallites in a pellet.

Second, the molecules associated with the acid sites in this example, those desorbing at >650 K, are not mobile at <650 K. Even if the strong acid sites differ energetically, one should expect that adsorbate pulses exposed to the sample at <650 K will populate a constant fraction of each type of site. For example, the first pulse might saturate all strong sites in the crystallites at the top of the bed, with subsequent pulses saturating lower layers. The implication is that it is probably not possible to measure a distribution of site strengths in this particular example, but that one should expect the differential heats to be constant up to a coverage of one per Al, even if energetically different sites exist. We will come back to this example later when we discuss consistency checks.

6. Effect of sample geometry

We will, here, consider in more detail the effect of sample geometry on the time necessary to achieve adsorption equilibrium. First, while the sample is usually held in vacuum prior to admission of a pure dose of adsorbate gas, there are circumstances, such as in measurements with adsorption mixtures [7,8], where a second component is present in the system. While hydrodynamic flow will dominate mixing processes for pure component systems, diffusion is the primary driving force in mixtures. The time constant associated with gas-phase mixing is l^2/D, where l is the length scale required for mixing D the diffusivity. Since typical gas-phase diffusivities are $\sim$0.1 cm^2/s, a length scale of 10 cm will result in a time constant of 1000 s, which is typical of the time required to make the adsorption measurement and, therefore much too long. More generally, the criterion for adsorption mixtures is:

$$l^2/D < t.$$

Second, even for adsorption in vacuum, the migration of molecules must proceed: (1) within a given particle or crystallite and (2) down the sample bed. Similar to what is found in TPD, where desorption temperatures for the same adsorbate on the same sample can change by 150°, depending on how the measurements are made [16,17], the system configuration will strongly affect equilibration times in calorimetry. Equilibration times for migration in the bed are *not* given by length^2/diffusivity, as in the gas phase because of coupling between desorption, adsorption, and diffusion. The equations describing migration throughout the sample bed are similar to those which describe TPD from packed beds. Of relevance to our situation is the fact that the observed desorption rate in a vacuum, which is what really controls equilibration, is less than the intrinsic desorption rate by a factor equal to the ratio of adsorption rates to diffusion rates [13,14]. For migration within a particle, this ratio is:

$$\pi^2 D_{\mathrm{p}}(\alpha\rho k_{\mathrm{ad}} R^2)$$

where $\alpha\rho$ is the surface area per volume of adsorbent, k_{ad} the adsorption rate constant, R the radius of the particle and D_{p} the diffusivity within the adsorbent. Typical experimental parameters make this ratio $\sim 10^{-6}$ and smaller. A similar [13,14] term is important for "diffusion" from particle to particle, except that R would be replaced by the length of the bed. Since the time for equilibration will vary in direct proportion with this ratio, it is clear that one must keep the length scales for adsorption, both sample particle size and bed length, as short as possible. For example, changing the bed height from 0.1 to 1.0 cm could change the equilibration time by a factor of 100. We refer the reader to other examples of the impact of diffusion on calorimetric design [18,19].

7. Equilibrium condition

Even for equilibrium adsorption, one may still not titrate the sites in reverse order of the energies if the energy difference between sites is too small. Under these conditions, both weak and strong sites will be populated simultaneously at finite temperatures. Fig. 3 shows a calculation of the differential heats that would be measured as a function of coverage at different adsorption temperatures, for a two-site Langmuir model [20]. In this calculation, 20% of the sites are considered to have adsorption energies of 20 kJ/mol and 80% to have 15 kJ/mol, and the adsorption entropy is assumed to be the same for both types of sites. At 0 K, one would obtain a step function in the heats, if equilibrium could be achieved. There will, however, be significant curvature for the observed

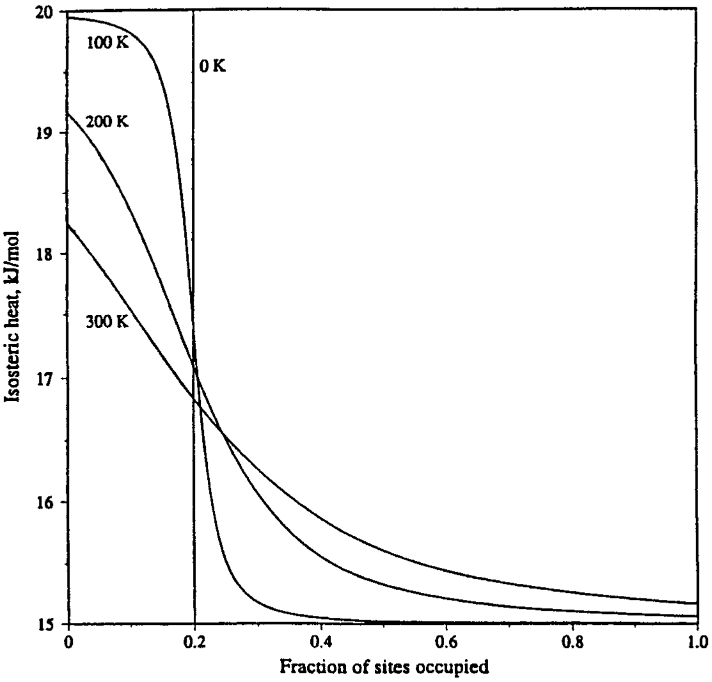

Fig. 3. Isosteric (q_{st}) heat of adsorption vs. coverage for a two-site Langmuir model with no interactions and 20% of the sites having a q_{st} of 20 kJ/mol and 80% of the sites having a q_{st} of 15 kJ/mol.

heats at high temperatures. The lesson is, of course, that heats which fall gradually with coverage may not be the result of a distribution of sites.

8. Heat-transfer rates

Evidently, it is critical that the heat associated with the adsorption process pass through the thermopiles to the heat sink. Because some rate of heat loss is inevitable, the total heat collected is optimized by increasing the rate of heat collection, as well as minimizing the heat losses. Since designing the sample cell for minimal heat loss rates will affect heat collection rates, the optimal design requires consideration of both factors. It should also be noted that increasing the rate at which heat is collected increases the signal from the calorimeter as well as the rate at which data can be collected. These factors are very important for most applications.

Usually, most of the resistance to heat transfer will occur in the sample bed itself. Picturing the physical process as involving transient heat transfer in a one-dimensional bed, the characteristic time constant for heat flow is:

$$l^2 \rho C_p / k$$

where ρ is the density of the sample, C_p the heat capacity, and k the thermal conductivity. Again, the dependence of the time constant on square of the characteristic-length scale suggests that one must minimize this quantity. (It is noteworthy that the length scale associated with heat transfer to the thermopiles may not be the same as that for adsorption on the sample as, for example, in a cylindrical sample geometry, where adsorption is likely to occur in an axial direction while heat transfer will occur radially.) Due to the fact that the thermal conductivity of a powder in vacuum can be very low, the time delay associated with the thermal process can be quite important although it is often, in our experience, not as severe as the time associated with adsorption equilibrium. Including an inert gas, such as He, with the sample to promote heat transfer may be helpful, although this can lead to trouble with mixing in the gas phase as discussed earlier.

The material used to construct the sample cell, along with the thickness of the cell, can also be important. For the sample geometry of Fig. 1, heat can potentially flow up the walls or out the thermopiles. To minimize heat losses up the walls, it is desirable that the walls be as thin as possible. The thermal conductivity of the construction materials should be reasonably high, or else other heat losses in the gas phase or due to radiation will become important.

As discussed earlier, radiation losses can potentially be important if the temperature rise due to adsorption at the top of the bed is significant and there is a line of sight between the hot sample and regions of the calorimeter in which the heat is not collected. An expected symptom of this problem is that, for strong adsorption in which molecules adsorb chromatographically down the bed, one will see heats that rise with increasing adsorbate pulses. This is due to radiation heat losses being most important for the initial doses, since the temperature rise will be at the top of the bed. In subsequent pulses, radiation losses will be screened by the top of the bed. This can be remedied, in case of the present problem, by having glass chips over the sample to absorb radiative heat losses. In gas mixtures, the glass chips may also limit heat losses due to free convection in the gas phase. The use of heat shields to inhibit both radiation and free convection in calorimetry, as well as an extensive review of the effect of calorimetric design on heat transfer, has been covered by Ginnings [21].

It is important to observe that we have only considered nonisothermal calorimeters in which a finite temperature rise occurs in the sample. This type of instrument is often referred to as an isoperibolic calorimeter, since the goal is to keep the heat-sink temperature constant, thereby fixing one temperature in the driving force for the heat flux. This is to be distinguished from techniques which use thermopile-like devices to induce a Peltier effect [2], keeping the sample temperature nearly constant.

9. Consistency checks

For any calorimeter design, it is important to demonstrate consistency in the results. Obviously, the differential heats should be independent of the dose size over a reasonable range and a plot of differential heat as a function of coverage should be independent of sample size. However, a more stringent test can be obtained from measuring differential heats for an adsorbate which has limited mobility at the temperatures used in the measurement. Under these conditions, sequential adsorbate pulses will populate different parts of the sample bed. One should observe a constant differential heat up to the point at which all the sites are saturated.

The adsorption of pyridine in H-ZSM-5 is a prototypical example. As shown by the TPD-TGA results in Fig. 2, pyridine adsorbed at the acid sites in one part of the sample will not be able to migrate to other parts of the sample in reasonable times below 600 K. The differential heats should, therefore, be independent of coverage until all sites in the bed are populated, even if all sites are not equivalent. Results which demonstrate this constant heat are presented in Fig. 4, which shows the differential heats as a function of coverage for four different H-ZSM-5 samples [22,23]. In each case, the differential heats are constant at ~200 kJ/mol up to a coverage of one per Al. The constant differential heats at lower coverages only provide an average differential heat for all acid sites in each sample. The fact that the average differential heat is the same on four different samples with widely varying Al contents may suggest that the sites are indeed energetically identical, although this is difficult to prove. By contrast, if a few sites, less than half the number which

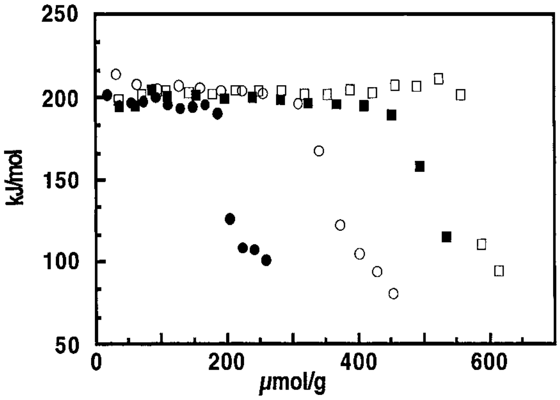

Fig. 4. Differential heats of adsorption for pyridine on four different H-ZSM-5 samples. The Al contents were 180, 370, 530, and 600 µmol/g. This figure is taken from Ref. [23].

desorbs at <650 K in Fig. 2, showed higher heats, one should be suspicious.

10. Calibration

Calibration of absolute heats is nontrivial. Methods commonly used in differential scanning calorimetry, such as measuring a heat of fusion for some standard, are not easily applied to isothermal calorimetry. While a large number of other methods have been suggested [1,2], including measurement of the baseline shift in the signal from the thermopiles upon passing a current through a Pt wire placed between the sample cell and the thermopiles [6,14], ultimate calibration requires measuring the differential heats of adsorption of a known system [5,21,8]. The ability to achieve accurate calibrations via resistive heating is covered extensively by Ginnings [21]; however, it has been our experience that it is nontrivial to reduce calibration errors below ±5% with this method. The approach that, we believe, provides the most accurate calibration is the use of a known, independently measured, thermodynamic quantity, such as the isosteric heat of adsorption measured by adsorption isotherms [5].

11. Summary

Calorimetric measurements can be significantly influenced by the design and operation of the instrument. Careful consideration of the design parameters such as the pertinent length scales for mass and heat transfer and the use of complimentary techniques, such as TPD, to obtain information on adsorbate mobility can be used to shorten the time to reach equilibrium and/or provide insight into the meaning of the collected data.

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