

GAS-SOLID EQUILIBRIA IN POROUS MATERIALS: A NEW MODEL

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INTRODUCTION

A new model for analyzing gas-solid equilibria in porous materials has been developed. Adsorption experiments with several probe gases and a commercial carbonaceous adsorbent have been analyzed using a multiple process adsorption model in which the capacity of each process, i , is calculated in millimoles per gram of adsorbent ($n_{i,ads}$) and the equilibrium adsorption constant for each process i is given as $K_{i,ads}$. The associated enthalpies of adsorption ($-\Delta H_{i,ads}$) were determined from adsorption measurements conducted at multiple temperatures via the van't Hoff equation. Since the values of $n_{i,ads}$ for each process are temperature independent, adsorption at other temperatures introduces only new $K_{i,ads}$ values.

The effects of porosity and surface area on the adsorptive properties of porous materials should be considered when selecting a porous material as an adsorbent. Work in our laboratory has shown that in catalyst doped adsorbents, small pores tend to concentrate reagents providing for better catalytic activity. An understanding of the pore size distribution and accessible surface area of solids is useful in selecting a suitable porous material for the adsorption of gaseous and liquid substrates. The BET equation has been the standard for many years in the determination of the surface area of porous materials. Although generally accepted, the BET equation has limitations, and as a result, has received some criticism in recent years. Our research efforts have been focused on developing a new gas-solid equilibrium model which is capable of providing information into the adsorption capacity of porous materials as well as thermodynamic data corresponding to the enthalpies of adsorption and equilibrium constants for adsorption of various sorptives.

EXPERIMENTAL

Approximately 0.3g of Amborsorb[®]572, a commercially available carbonaceous adsorbent, was degassed ($<10^{-4}$ torr) for a minimum of 8 hours at 200°C prior to each adsorption experiment. The sorptives chosen were selected to encompass a wide range of properties. Nitrogen, CO, and CH₄ are non-condensable adsorptives at the temperatures examined and are non-polar, polar and polarizable sorptives, respectively. Propane, SO₂, and NH₃ are condensable sorptives at the temperatures studied and are polarizable, acidic, and basic, respectively. All gases were of 99.99% purity and required no further purification. Gaseous uptake measurements were performed on a Micromeretics ASAP 2000 analyzer using a 36 point pressure table ranging from 1 torr to 760 torr. Low temperature adsorption measurements were performed with the aid of solvent / liquid N₂ baths to give the desired temperature.

RESULTS AND DISCUSSION

Adsorption measurements to determine porosity and surface area of porous materials have long been evaluated by the BET equation ⁴(Equation 1)

$$\frac{x}{n(1-x)} = \frac{1}{CN_m} + \frac{(C-1)x}{CN_m} \quad (1)$$

where n = moles of gas adsorbed, N_m = total moles adsorbed, and $x = P/P^0$ with P = equilibrium pressure in torr and $P^0 = 760$ torr. The values N_m and C are obtained from a linear plot of $x/n(1-x)$ vs x . The equation is only applicable in a pressure range of 0.05 to 0.3 torr. The BET C constant (Equation 2) is a complex quantity related to the equilibrium constant for monolayer adsorption ($K_{i,ads}$) and multilayer adsorption ($K_{j,ads}$) along with

$$C = \frac{K_{i,ads}}{K_{j,ads}} \exp\left(\frac{Q_{mono} - Q_{multi}}{RT}\right) \quad (2)$$

contributions from the enthalpy of adsorption of the monolayer (Q_{mono}) and multilayer (Q_{multi}). The components of Equation 2 are not resolved, so C is difficult to interpret.^{2,3}

Our research has focused on the development of a multiple process adsorption model¹ which is applicable over a wider pressure range and is presented in Equation 3. The adsorption isotherm is resolved into individual adsorption processes (n_i) and equilibrium constants for adsorption ($K_{i,ads}$) for those processes using Equation 3.

$$N_{total} = \sum_i \frac{n_i K_i [P]}{1 + K_i [P]} \quad (3)$$

Here N_{total} = total moles adsorbed per gram of solid, P = relative equilibrium gas pressure in torr, n_i = number of millimoles of process i , and $K_{i,ads}$ = the equilibrium constant for adsorption for process i . From the equilibrium constants calculated from multiple temperature adsorption experiments, a direct thermodynamic measure of the enthalpy of adsorption, $-\Delta H_i$, for each process can be calculated. Table 1 lists the $n_{i,ads}$ values and corresponding equilibrium constants ($K_{i,ads}$) that have been calculated from our multiple process adsorption model. One can see in the values for $K_{i,ads}$, that as the polarizability of the sorptive increases so does the affinity for adsorption. Table 2 lists the enthalpies for the adsorption processes, $-\Delta H_{i,ads}$ that have been calculated based on the temperature dependency of $K_{i,ads}$. One can see that the calculated enthalpies are greater than the reported heats of vaporization of the gases and that they fall within the accepted range for physisorption processes (2-12 kcal/mol).

Once the best n_i and K_i values for each process have been determined by a modified Simplex fitting routine capable of fitting multiple temperature adsorption data, the adsorption isotherm can be separated into the individual adsorption processes. Figures 1 and 2 show the individual adsorption processes for propane and methane adsorption by Amborsorb[®] 572 at 25°C. Three adsorption processes were found to be occurring at the same time, however, process 1, which corresponds to filling the smallest accessible pores, finishes before the entire adsorption process is complete. It should be clarified that the pores accessible to the sorptives will depend on the size of the probe, and that not all of the pores accessible to CH_4 will be accessible to propane.

In contrast, standard N_2 porosimetry analysis at 77K reports a micropore volume of 0.45 ml for A-572. If one multiplies the $n_{i,ads}$ values obtained for propane and methane adsorption by the corresponding molar volumes of the sorptives, one gets 0.41 ml for the total adsorption process for propane, and 0.25 ml for the total adsorption process of methane. The results indicate that the multiple process adsorption model may be able to distinguish pore size distributions in the reported micropore region of porous materials.

CONCLUSIONS

A multiple process adsorption model has been developed to analyze gas-solid equilibria in porous materials. From this model, one is able to calculate the number of millimoles ($n_{i,ads}$) and the corresponding equilibrium constants ($K_{i,ads}$) for each adsorption process. Enthalpies of adsorption ($-\Delta H_{i,ads}$) for each process can be calculated from the temperature dependency of $K_{i,ads}$. In contrast to the standard BET approach, this multiple process adsorption model has the potential for distinguishing the micropore distribution in porous materials as well as providing important thermodynamic data not readily obtainable from the BET method.

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Table 1: Equilibrium Adsorption Parameters for A-572						
T(°C)	n ₁	n ₂	n ₃	K ₁	K ₂	K ₃
		(mmol/g)				
	N ₂					
-93	0.322	1.68	5.38	124.5	11.46	0.8587
-42				5.739	.9214	.1213
0				1.068	0.2065	0.0423
25				0.6992	0.045	0.045
	CO					
-93	0.5138	1.934	5.325	204.9	16.53	1.169
-42				8.448	1.112	0.1455
25				0.4704	0.058	0.058
	CH ₄					
-43	0.17750	1.427	5.037	153.4	13.71	0.996
0				15.98	2.07	0.238
25				4.91	0.876	0.111
40				3.24	0.563	0.0803
	C ₃ H ₈					
25	1.02	2.46	2.008	2704	62.5	3.3
40				947	29	1.75
55				410.6	15.2	0.97
75				158.4	7.12	0.48
	SO ₂					
25	0.932	4.75	6.21	364.6	11.83	2.81
40				136.2	6.15	1.42
55				66.3	3.44	0.81
75				29.4	1.6	0.416
	NH ₃					
40	0.2389	0.800	1.410	1903	17.51	0.3193
55				581.6	8.339	0.2048
75				143.4	3.237	0.1214

Table 2: Enthalpies of Adsorption for A-572 (kcal/mol ± 0.5 kcal/mol)			
	H ₁	H ₂	H ₃
N ₂	-4.78	-4.74	-2.82
CO	-5.48	-5.08	-2.74
CH ₄	-6.74	-5.51	-4.37
C ₃ H ₈	-11.68	-8.96	-8.05
SO ₂	-10.32	-8.22	-7.83
NH ₃	-14.14	-6.43	-6.16

Figure 1: Propane Adsorption by A-572
25°C

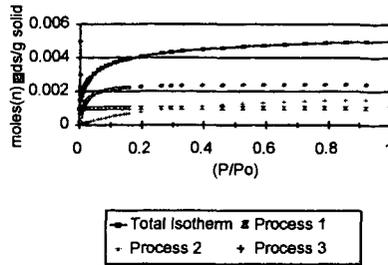


Figure 2: CH₄ Adsorption by A-572
25°C

