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Gas/vapor flow microcalorimetry on porous carbons II. Heat of adsorption of toluene on microporous/mesoporous carbons[1]

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Abstract

The heat produced by incremental adsorption of toluene vapor on two activated carbons has been investigated by flow microcalorimetry (FMC). One carbon is primarily microporous with 85% of its pore volume associated with micropores, whereas, mesopores account for 75% of the pore volume in the second carbon. Both integral and molar heats have been determined for adsorption of toluene in a partially filled pore system in the pore fill fraction range from 0.5 to 0.95. The carbon samples were diluted with polytetrafluoroethylene powder in order to improve the flow/heat transfer characteristics of the system and decrease the thermal response time of the calorimeter. Thermal response profiles were de-convoluted in order to relate the time evolution of the response to dynamic adsorption processes. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Heat of adsorption; Flow microcalorimetry; Activated carbon

1. Introduction

Flow microcalorimetry (FMC) has been developed as a simple, effective technique for characterizing solid, high surface area adsorbents in both liquid and vapor environments [1]. It complements adsorption isotherm studies, and as a technique to assess enthalpy effects it is more convenient to apply than traditional dosing calorimetry. Recently FMC has been used in combination with isotherm data to determine the integral and molar heats of adsorption of toluene vapor on a high capacity, microporous adsorbent carbon [2]. The results were limited to an isotherm region (pore fill fraction 0.5–0.95) where adsorption was relatively independent of adsorptive concentration. In this prior investigation, the degassed carbon was exposed to relative pressures in the range from 0.001 to 0.1 until adsorption equilibrium was reached in the fill fraction range indicated. Extending the FMC technique to several adsorbent carbons with varying degrees of microporosity/mesoporosity showed that the thermal response profile, i.e., the rate of heat evolution with time at a fixed concentration of adsorptive vapor produced a characteristic ‘fingerprint’ for each carbon [3]. In the current investigation, sorption kinetics as a function of pore size distribution was probed at 383.6 K by first saturating all micropores and most mesopores of selected

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carbons by equilibration with toluene vapor at a relative pressure of 0.004, followed by partial desorption of adsorptive upon exposure of the carbon to a pure nitrogen stream for a preselected time. Subsequent exposure to adsorptive produced a second exotherm associated with adsorption into the pore space generated by the prior desorption process. Adsorption thus took place in increments on a carbon in the fill fraction range from 0.5 to 0.95.

2. Experimental

2.1. Materials

BPL activated carbon, supplied by Calgon, is predominantly microporous, having a N_2 BET surface area of 1200 m^2/g and pore volume of 0.72 ml/g, with 85% of this volume associated with pores <2 nm in size[2]. Westvaco A1100, supplied by Westvaco, is a mesoporous carbon with a N_2 BET surface area ca. 1700 m^2/g. Its total pore volume is 1.2 ml/g of which 75% is in the pore size range between 2 and 50 nm[3]. Fisher scientific ACS-certified grade toluene is the adsorptive and Matheson zero gas nitrogen is the carrier gas. Polytetrafluoroethylene (PTFE) powder was obtained from Aldrich Chemicals (18, 247-8).

2.2. Flow microcalorimetry

Heats of adsorption under various conditions were determined using a Microscal Flow Microcalorimeter, which has been described previously [1,4]. The microcalorimeter was placed in a constant temperature chamber controlled with a World Precision Instruments Air-Therm Heater Controller to ±0.1°C. A Bronkhorst F201C-FD Mass Flow Meter/Controller supplied a pure nitrogen stream of 6.55 ml/min, which was employed to outgas the fresh sample (16–24 h at 383.6 K), and desorb toluene adsorbate. A Bronkhorst F200C-FD Mass Flow Controller supplied a nitrogen stream that was saturated with toluene at temperatures in the range 274–293 K. The stream could be diluted with nitrogen, supplied by an MKS Type 1259C Mass Flow Controller, to provide toluene concentrations in the range 1.3–109.3 mg/l at a flow rate of 6.55 ml/min and 299 K. At 383.6 K, this corresponds to toluene relative pressures ranging from 3.0×10^{-4} to 2.5×10^{-2} after correcting for temperature assuming ideal gas behavior.

The carbon was mixed with PTFE powder in the proportion 1 part carbon to 9 parts PTFE to improve the flow characteristics of the calorimeter and reduce the thermal response time. After outgassing the carbon sample (25 mg) for 16–24 h in the pure nitrogen stream, adsorption in the high fill fraction range was investigated using the following procedure: a computer controlled four-way valve was employed to direct a toluene/nitrogen mixture of known concentration (C_0) into the sample chamber where adsorption occurred. The accompanying exotherm was recorded as a function of time by the calorimeter thermistors. After 30 min to several hours, depending on the toluene concentration, the thermal response returned to the baseline, signifying attainment of adsorption equilibrium. At this point the adsorptive concentration downstream of the calorimeter, measured with an HNU DL-101 photoionization detector (PID), reached C_0. At this steady-state, switching to the pure nitrogen stream gave an endotherm proportional to the amount of toluene desorption, and a PID measurement of desorbing molecules. Initially, desorption was allowed for 5 min after which a second adsorption was initiated by switching to the toluene/nitrogen stream again. At the steady-state resulting from this process, a second desorption was conducted for 9 min followed by a third adsorption. Successive desorption/adsorption cycles were carried out up to a maximum desorption time of 24 h. Since the system attained equilibrium in each adsorption step, the amount of toluene adsorbed equaled the amount of adsorbate lost in the preceding desorption step. Although the area (and heat content) of each endotherm and the corresponding exotherm that follows are approximately equivalent, the latter can be determined more precisely and is emphasized in this study. For each run, a thermal calibration pulse of known energy was produced by resistive heating in the sample cell allowing the measured adsorption/desorption response to be expressed in energy units (J/g) [2]. The amounts adsorbed over the same relative pressure range and the same temperature were also

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[2] Technical Data Sheet supplied by Calgon Carbon Corporation.

[3] Technical Data Sheet supplied by Westvaco Charleston Research Center.

obtained from the equilibrium adsorption isotherm, determined gravimetrically with a Cahn D200 microbalance system using a similar vapor flow system [5]. Outgassing conditions employed in the gravimetric studies were the same as those used in the FMC experiments.

3. Results and discussion

A typical FMC thermal response trace obtained from toluene vapor adsorption/desorption on WV A1100 activated carbon/PTFE at 383.6 K using the above procedure is shown in Fig. 1. The initial exotherm, representing adsorption saturation, is followed by four desorption/adsorption cycles where the desorption time is increased successively. The sixth exotherm is a 600 mJ calibration pulse from the resistive heater. The thermal response is assumed to be entirely associated with adsorption on the carbon in all the reported results since adsorption on PTFE is negligible. Exothermic (adsorption) responses are shown in Fig. 2 for the WV A1100 carbon compared to the full (saturation) response. Similar responses are shown for toluene vapor adsorption on the BPL carbon/PTFE at 383.6 K in Fig. 3. The heat contents of the thermal response peaks shown in Figs. 2 and 3 are listed in Table 1 at each desorption time that precedes the adsorption response. The heat content of the endotherm that precedes each exotherm is also listed as a heat of desorption in Table 1 for comparison. The full saturation responses (241.9 J/g and 194.0 J/g) in conjunction with adsorption isotherm data [2] yielded 96.7 kJ/mol and 102 kJ/mol for the molar heats of adsorption of toluene on BPL and WV A1100 carbons, respectively. For reference, ΔH_{vap} for toluene is 38 kJ/mol. Molar heats of adsorption were not determined for the exotherms that followed. An estimate of the amount adsorbed could not be accurately determined for these exotherms due to adsorption taking place in the ‘flat’ portion of the adsorption isotherm. As the desorption time becomes longer, desorbed molecules are presumably increasingly removed from micropores, in accord with the inverse dependence of adsorbate–adsorbent interaction energy with pore diameter [6]. Consequently, as the areas of the sequential exotherms in Figs. 2 and 3 become larger, there is

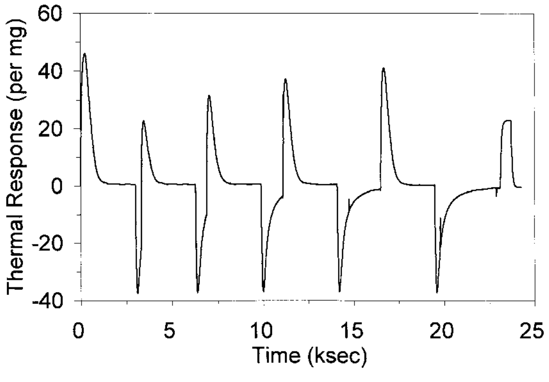

Fig. 1. Adsorption/desorption responses with variable desorption times (toluene on WV A1100 carbon at 383.6 K, $P/P_0 = 0.004$).

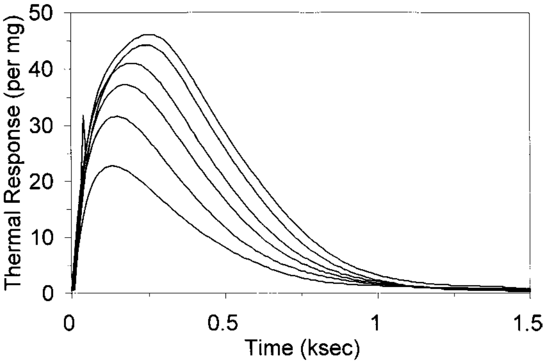

Fig. 2. Adsorption responses after variable desorption times (toluene on WV A1100 carbon at 383.6 K, $P/P_0 = 0.004$).

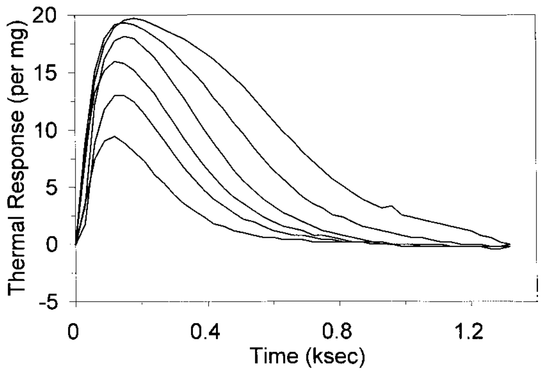

Fig. 3. Adsorption responses after variable desorption times (toluene on BPL carbon at 383.6 K, $P/P_0 = 0.004$).

Table 1
Incremental integral heats of adsorption and desorption (toluene on BPL and WV A1100 carbons at 383.6 K and $P/P_0 = 0.004$)

BPL carbon		WV A1100 carbon	
Desorption time (min)	Heat of adsorption/desorption (J/g)	Desorption time (min)	Heat of adsorption/desorption (J/g)
5.5	52.6/53.0	5.7	72.5/71.2
10.0	81.9/87.1	10.5	104.3/104.1
20.5	113.1/125.1	20.2	133.0/132.7
40.0	140.3/168.1	40.2	153.9/155.6
209.0	189.4/197.2	80.2	165.9/156.3
1440	241.9	180	174.8/187.5
		960	194.0

increasing probability that adsorption in narrower pores is making a significant contribution. Resolution of the overall exotherm was attempted to determine whether it represents a summation of two or more distinct thermal processes. The calorimeters' time-dependent heat rise and cooling response to a pseudo instantaneous energy input was modeled by introducing an ohmic calibration pulse for several seconds. The resultant exotherm is well described by a single exponentially modified Gaussian function independent of pulse magnitude over the range of experimentally observed adsorption exotherms. Analysis of the sequential exotherms for BPL carbon in Fig. 3 with peak fitting software (Microcal Origin) showed that the small response peaks could be fitted to a single exponentially modified Gaussian peak but as the response increased at longer desorption times, a good fit could only be obtained using two exponentially modified Gaussian peaks. De-convolutions of the smallest and largest response peaks in Fig. 3 are shown in Fig. 4, illustrating a typical one and two peak fit. The position of the resolved peak maxima are independent of peak size, with peak 1 at 105 s and peak 2 at 400 s. Fig. 5 shows the areas for peak 1 and peak 2 for each exotherm in Fig. 3 plotted versus the adsorption heats listed in Table 1. Initially only response peak 1 is present but its intensity levels off below 100 J/g when response peak 2 first appears at low intensity. At higher adsorption heats (i.e., longer desorption times) the intensity of response peak 2 continues to increase. Conversely, the sequential exotherms up to 194 J/g for mesoporous WV A1100 carbon shown in Fig. 2 could all be fitted to one exponentially modified Gaussian peak with the maximum increasing from 125 s to 250 s as the desorption amount increased. These peak areas are shown in Fig. 6. The heat contents in peaks 1 and 2 for each integral heat of adsorption for BPL carbon (Table 1) are listed in Table 2.

Table 2
Heat content of peaks 1 and 2 (toluene on BPL carbon at 383.6 K and $P/P_0 = 0.004$)

BPL carbon	
Peak 1 (J/g)	Peak 2 (J/g)
52.6	0
81.9	0
92.9	20.1
96.5	43.8
97.4	92.0
98.5	143.3

The nature of the resolved exotherms in conjunction with the known micro- and mesopore content of the carbon adsorbents indicates that the thermal response peaks obtained in flow microcalorimetry have an initial response due to adsorption in the more easily accessed wider pores, i.e., mesopores, followed by a slower response due to the diffusion of adsorbate molecules into less easily accessed narrow pores, i.e., micropores. Thus the overall adsorption response of the BPL carbon can be represented by one peak for short desorption times (<20 min) when only mesopores are available but requires two peaks for longer desorption time whereby partial depletion of adsorbate from micropores occurs. WV A1100 shows only one peak even after 16 h desorption due to the very low

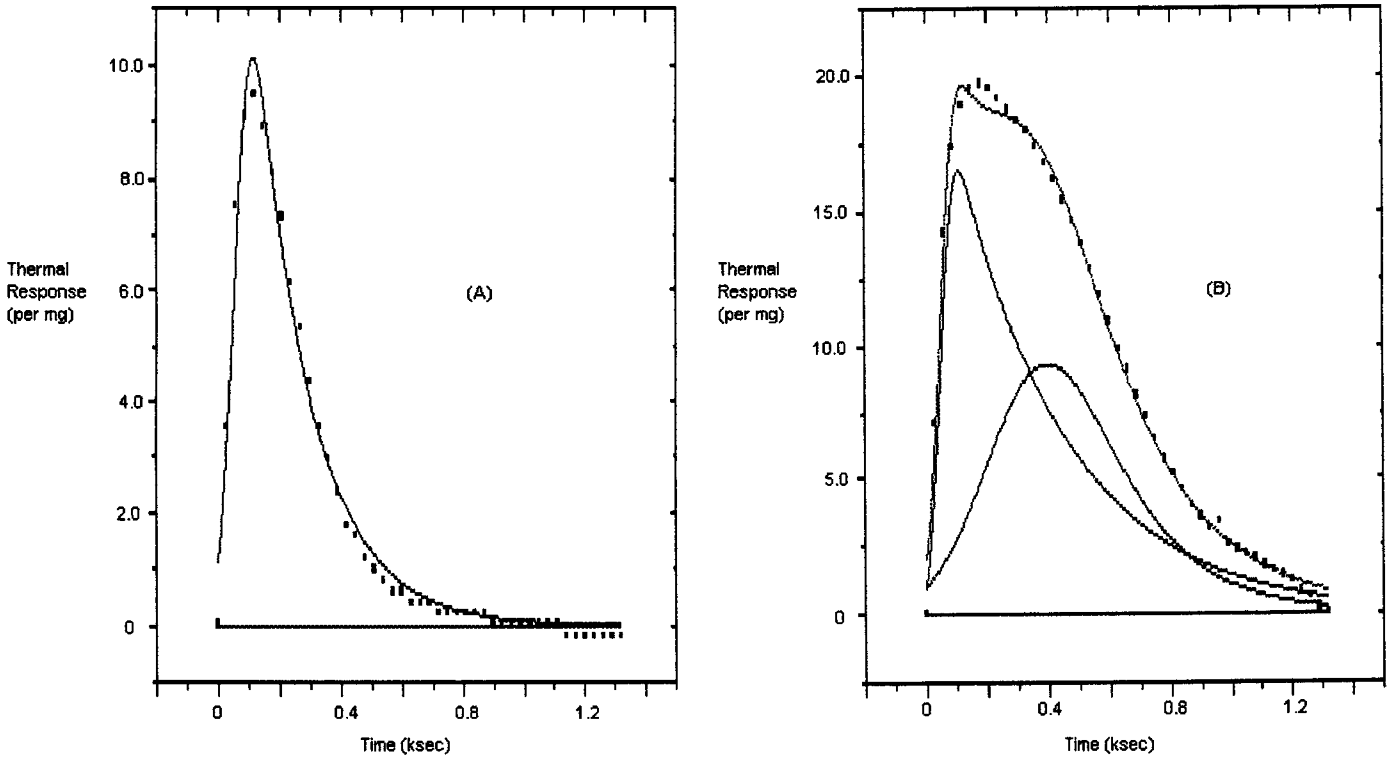

Fig. 4. Typical de-convolution of two response profiles in Fig. 3.

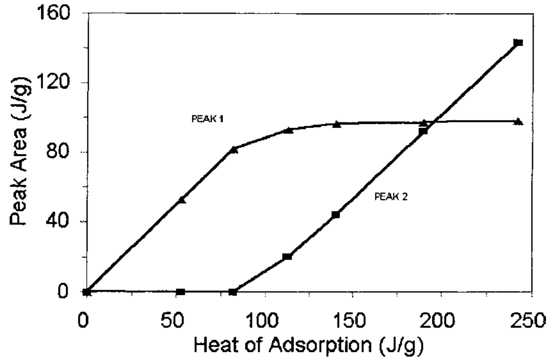

Fig. 5. Peak areas 1 and 2 vs. heat of adsorption (toluene on BPL carbon at 383.6 K, $P/P_0 = 0.004$).

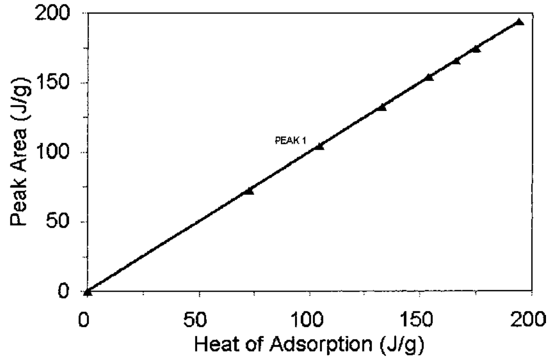

Fig. 6. Peak area 1 vs. heat of adsorption (toluene on WV A1100 carbon at 383.6 K, $P/P_0 = 0.004$).

micropore volume of this predominantly mesoporous carbon.

4. Conclusions

Flow microcalorimetry studies on microporous/mesoporous carbon adsorbents indicate that the exotherm due to the adsorption of toluene molecules can be de-convoluted into separate heat effects associated with pore size-dependent adsorption processes. The initial process is adsorption in more easily accessed mesopores. Adsorbed molecules in the mesopores then migrate into micropores, a more thermodynamically stable state, producing a second thermal response which dominates the overall exotherm in adsorbents where a major fraction of the pore volume is associated with micropores.

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