FMC THERMAL RESPONSE PROFILES FROM VAPOR ADSORPTION ON POROUS CARBONS

P. J. Reucroft and D. Rivin
Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY 40506 and U.S Army Soldier Systems Command, Natick RD&E Center, Natick, MA 01760-5019

Introduction

Flow microcalorimetry (FMC) is a simple, effective technique that allows the adsorption energetics of solid, high surface area adsorbents to be determined in both liquid and vapor environments (1). FMC generally complements and extends traditional adsorption isotherm studies and has the advantage of being more convenient to apply than techniques such as adiabatic calorimetry. A number of studies reported in the literature have focused on applications involving the integral heat of adsorption (expressed in J/g of adsorbent) determined in an isotherm region where adsorption is relatively independent of adsorptive concentration (2-4). Other investigators have simultaneously determined the number of molecules adsorbed and evaluated the molar heat of adsorption (5). The selectivity, capacity and kinetics of molecular sieve adsorbents have also been studied by FMC techniques (6). In general, a wide variety of applications have been explored (7). Several types of adsorbent have been investigated by FMC, including activated carbons. There has generally been a paucity of studies on microporous/mesoporous carbons, however, and detailed studies on the time evolution of the FMC thermal response are lacking. The objective of the present investigation has been to characterize the FMC thermal response to toluene vapor of several novel, high capacity, activated carbon adsorbents with different pore distributions.

Experimental

Maxsorb AW20, was supplied by The Kansai Coke and Chemicals Co., Ltd. It has a high surface area (2330 m^2/g) and pore volume (1.07 ml/g): 45.3% associated with pores of diameter <1nm and 93.6 % associated with pores <2nm in diameter (8). Ambersorb 572 and 563 were supplied by Rohm and Haas. Ambersorb 572 (1100m^2/g) has 68% of its pore volume associated with pores of diameter <2nm and 31.7% of its pore volume associated with pores of diameter >2nm and <30nm. Ambersorb 563 (550m^2/g) has 62.2% of its pore volume associated with pores of diameter <2nm and 37.8% of its pore volume associated with pores of diameter >2nm and <30nm (8). Fisher Scientific ACS-certified grade toluene was the adsorptive and Matheson zero gas nitrogen was the carrier gas.

Thermal response profiles were determined using a Microscal Flow Microcalorimeter, which has been described previously (1,2). The Microcalorimeter was placed in a constant temperature chamber that was 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 (18 hours at 343K) 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 - 293K. The stream could be diluted with a pure nitrogen stream, supplied by a MKS Type 1259C Mass Flow Controller, to provide toluene relative pressures ranging from 1.0×10^{-3} to 8.4×10^{-2} at 343K . The thermal response profiles were determined by procedures that have been described previously (9).

Results and Discussion

FMC measurements on different carbons have shown that the thermal response profile as a function of time is generally characteristic of the carbon. Figs. 1 and 2 show the thermal response profiles of toluene vapor on Ambersorb 572 and 563, respectively. The limited studies conducted to date indicate that the characteristic profile obtained for a particular adsorbent appears to be independent of relative pressure and the nature of the adsorptive. Deconvolution of thermal response profiles such as these with peak fitting software showed that the overall thermal response can be broken down into several discrete thermal response processes that occur at different rates. Fig. 3 shows the thermal response profile of toluene vapor on Maxsorb AW20, deconvoluted into four discrete responses. A Gaussian profile was used to represent each peak and the Gaussian peaks shown provide the best "fit" to the data. Fig. 4 shows the areas of peaks 1 and 2, the areas of peaks 3 and 4 and the total response profile area plotted versus relative pressure. The area under peaks 1 and 2 tends to increase with increasing relative pressure but the area under peaks 3 and 4 is relatively constant with increasing relative pressure. This suggests that the thermal response associated with peaks 3 and 4 may be associated with adsorption in micropores (pores with diameter <2nm) and the thermal response associated with peaks 1 and 2 is possibly due to adsorption in mesopores (pores with diameter >2nm but <50nm).

Conclusions

FMC studies on several microporous/mesoporous carbons indicate that the characteristic thermal response profiles obtained may result from successive adsorption processes into the different pore size ranges. Additional studies are underway to further explore these effects and obtain definitive evidence for the involvement of pores in determining the response profile shape. New insight into the kinetics of vapor adsorption in porous carbons and how molecules re-arrange themselves in pore systems under dynamic conditions can potentially be obtained from such studies.

References

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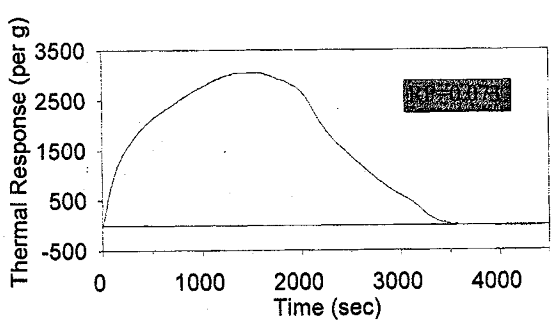

Fig 1. Thermal Response Profile (Toluene on Ambersorb 572 at 343K, Relative Pressure = 0.073).

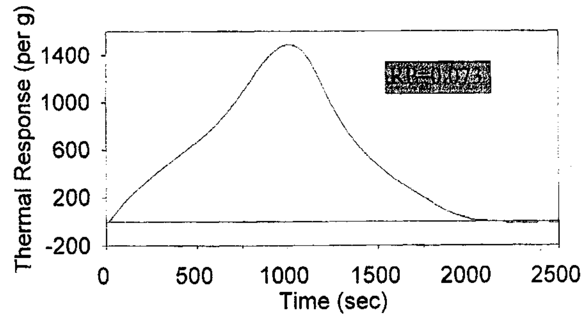

Fig.2. Thermal Response Profile (Toluene on Ambersorb 563 at 343K, Relative Pressure = 0.073)

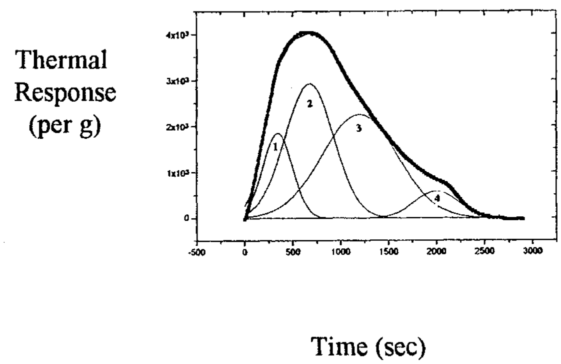

Fig 3. Deconvoluted Thermal Response Profile (Toluene on Maxsorb AW20 at 343K, Relative Pressure = 0.073)

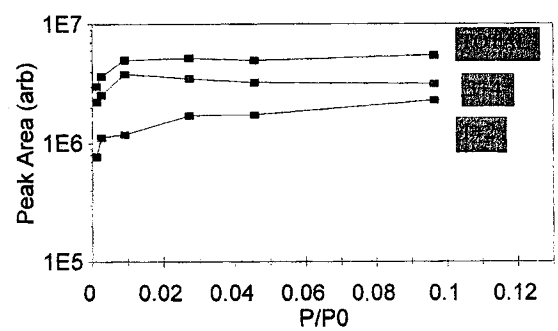

Fig. 4. Thermal Response Peak Areas versus Relative Pressure (Toluene on Maxsorb AW20 at 343K).