

HEAT OF ADSORPTION OF TOLUENE ON AMBERSORB 563

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Introduction

Flow microcalorimetry (FMC) [1] has recently been employed to investigate the heat of adsorption of toluene vapor on a series of microporous, mesoporous and non-porous carbon adsorbents [2-5]. Adsorption heats were measured at pore fill fractions that were either >0.5 [2-4] or <0.5 [5]. 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. The objective of the present investigation has been to determine the integral and molar heat of adsorption in the high pore fill fraction range of an activated carbon adsorbent that is microporous but has a significant fraction of its pore volume in the mesoporous range.

Experimental

The carbon adsorbent, Ambersorb 563, was supplied by Rohm and Haas. Ambersorb 563 (N_2 BET Surface Area = $550\text{m}^2/\text{g}$) has 62.2% of its pore volume associated with pores of diameter $<2\text{nm}$ and 37.8% of its pore volume associated with pores of diameter $>2\text{nm}$ and $<30\text{nm}$ [6]. 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 [1-5]. The Microcalorimeter was placed in a constant temperature chamber that was controlled with a World Precision Instruments Air-Therm Heater Controller to $\pm 0.1^\circ\text{C}$. 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 $274 - 293\text{K}$. 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 . Thermal response profiles were obtained by procedures that have been described previously [2]. For each run, a thermal calibration response 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 amount of toluene adsorbed at each relative pressure (P/P_0) was determined with a downstream detector (DSD) and by measuring the equilibrium adsorption isotherm at 343K [2].

Results and Discussion

Fig. 1 shows a typical thermal response profile produced by adsorbing toluene vapor at a relative pressure (P/P_0) of 0.073 on Ambersorb 563 at 343K . Studies conducted to date have indicated that the characteristic profile obtained for a particular adsorbent appears to be independent of relative pressure and the nature of the adsorptive. The integral heat of adsorption (in J/g) was determined from the thermal response profile using a thermal calibration response of known energy and the mass of the carbon sample. Integral heats of adsorption at several relative pressures are shown in Fig. 2. The dependence of the integral heat of adsorption on relative pressure is similar to the adsorption isotherm. This was also observed in the case of Maxsorb AW20, a microporous adsorbent [2]. The amount adsorbed, determined from the adsorption isotherm and also using the downstream detector, is shown in Fig. 3. The DSD amount adsorbed is consistently higher than the isotherm values. The two values approach each other at high relative pressures as before [2]. Combining the results from Figs. 2 and 3 yields the molar heat of adsorption. The molar heat of adsorption as a function of relative pressure is shown in Fig. 4. The molar heat of adsorption is approximately constant with relative pressure and yields an average value of 95 kJ/mole when the isotherm-determined amount adsorbed is used. The DSD determined molar heat of adsorption averages 60 kJ/mole due to the generally higher DSD determined amount adsorbed.

Conclusions

FMC studies on Ambersorb 563, a microporous carbon with a significant amount of porosity in the mesopore range, have shown that the molar heat of adsorption using FMC and isotherm determined adsorption amounts, is about 2.5 times higher than the heat of liquefaction of toluene [2]. The average value of the molar heat of adsorption (95 kJ/mole) is somewhat higher than

the corresponding value that was determined for Maxsorb AW20 (84 kJ/mole [2]) even though Maxsorb AW20 has a higher fraction of its pores in the micropore range. This suggests that there may be an additional affinity in the adsorptive interaction between toluene and Ambersorb 563 due to the polymeric origin of Ambersorb 563.

References

- [1] Groszek AJ. Selective adsorption at graphite/hydrocarbon interfaces. Proc. Roy. Soc. Lond. 1970; A314:473-498.
- [2] Reucroft PJ, Rivin D. Gas/vapor flow microcalorimetry on porous carbons I. Heat of adsorption of toluene on a microporous carbon. Carbon 1997; 35(8):1067-1071.
- [3] Reucroft PJ, Rivin D. FMC thermal response profiles from vapor adsorption on porous carbons. Extended abstracts, 23rd biennial conf. on carbon. Penn State Univ.(Pennsylvania, USA): American Carbon Society, 1997;122-123.
- [4] Reucroft PJ, Rivin D. Gas/vapor flow microcalorimetry on porous carbons II. Heat of adsorption of toluene on microporous/mesoporous carbons. Thermochim Acta; in press.
- [5] Reucroft PJ, Rivin D. Characterization of adsorbent carbons by FMC. ACS Division of Fuel Chemistry Symposia Preprints 1998; 43(4):785-789.
- [6] Technical Data supplied by Rohm and Haas.

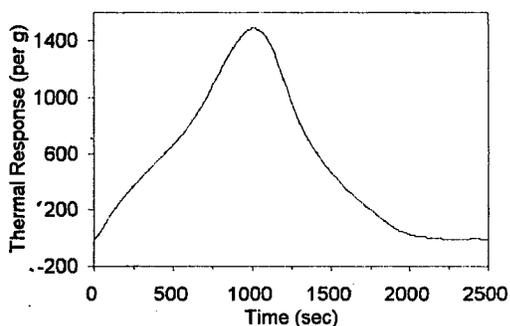


Fig 1. Thermal response profile (Toluene on Ambersorb 563 at 343K, Relative Pressure = 0.073).

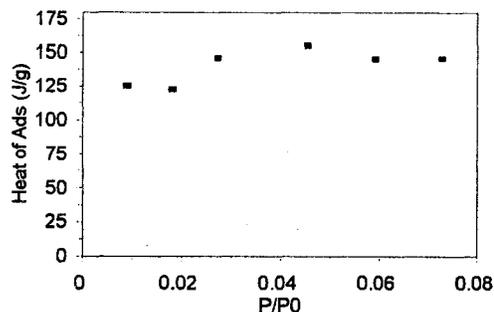


Fig.2. Integral heat of adsorption (Toluene on Ambersorb 563 at 343K)

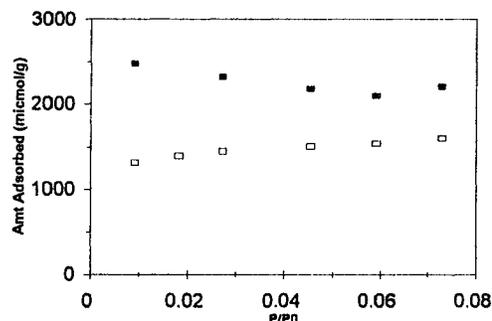


Fig 3. Amount adsorbed as a function of relative pressure (Toluene on Ambersorb 563 at 343K; ■ DSD, □ ISO)

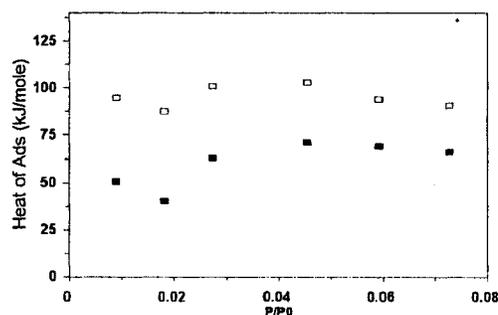


Fig. 4. Molar heat of adsorption (Toluene on Ambersorb 563 at 343K; ■ FMC/DSD, □ FMC/ISO).