

APPLICATION OF SOLID STATE NMR TECHNIQUES TO STUDIES OF ADSORPTION PROCESSES ON ACTIVATED CARBON

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Introduction

Though the adsorption of gases and vapours onto porous, activated carbon has been studied extensively by gravimetric and volumetric methods which are primarily used to elucidate the pore structure of the adsorbent, and by calorimetry, which provides information on active surface sites, little direct information is available on the dynamic effects occurring at the molecular level during the adsorption process.

The data described within have been derived as part of a programme to demonstrate the applicability of magic angle spinning (MAS) solid state NMR techniques to studies of various adsorbates on activated carbon. The work demonstrates that the techniques provide not only useful data concerning the bulk uptake of adsorbates [1], but also information on pore size distribution, dynamic processes and competitive adsorption effects, which occur during the adsorption process [2-5].

Experimental

NMR measurements were carried out on a Chemagnetics CMX200 MAS spectrometer. Water adsorption measurements were carried out with $^2\text{H}_2\text{O}$, monitoring the ^2H resonance at 30.721MHz. ^{31}P resonances were measured at 81.014 MHz with sample spin speed typically around 1.5KHz. Samples of BPL and SC2 carbon were obtained from Chemviron Carbon. Carbon characterisation was carried out by N_2 or CO_2 adsorption followed by BET or alpha-s analysis. Fuller experimental details are given in references 1 to 5.

Results

In all cases, whether water or organic adsorbates, the NMR spectrum was typified by a single sharp signal with chemical shift close to that for bulk adsorbate, with a broad peak shifted to lower frequency; magnitudes of the peaks depending upon loading. A simple experiment

(Figure 1) in which an SC2 carbon is increasingly loaded with trimethylphosphate (TMP) demonstrates the gradual filling of the pore system (low frequency peak) and the appearance of "free" TMP at high loadings. Additionally, when a nutshell carbon, successively activated to pore volumes 0.06, 0.22, 0.27 and $0.43 \text{ cm}^3 \text{ g}^{-1}$ was loaded to 40%w/w with $^2\text{H}_2\text{O}$ it clearly showed that the broad, low frequency peak increased in area. This phenomenon has been observed with all systems studied both by us and other workers [6], and the broad peak is thus attributed to adsorbate filling the pore system.

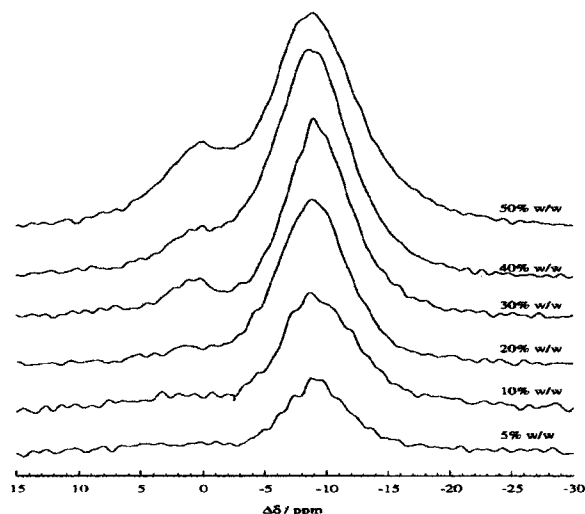


Figure 1: Static single-pulse spectra acquired for a variety of TMP loadings on SC2 carbon

The nature of the low frequency peak has been further probed by studying spin-lattice relaxation times as the peak is traversed. These data support the hypothesis that lower frequency components of the signal are associated with molecules tightly bound to the surface or constricted in very small pores.

The quantitative nature of this adsorption was readily demonstrated by measuring the adsorption isotherms of several adsorbates on carbon materials by

both gravimetric methods and MAS-NMR. A typical result is shown in figure 2 for adsorption of $^2\text{H}_2\text{O}$ on unaged BPL carbon.

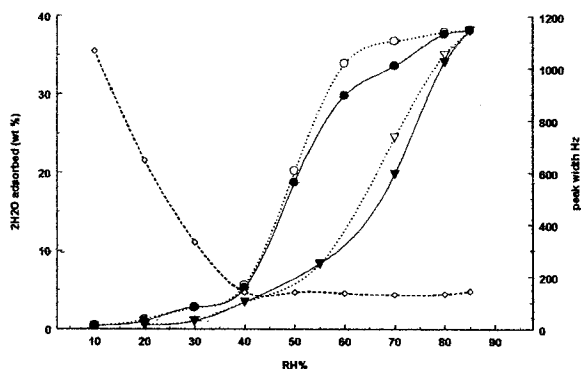


Figure 2: Adsorption of $^2\text{H}_2\text{O}$ adsorbed on unaged BPL carbon. NMR data shown in solid lines, gravimetric data in dotted lines.

The ability to differentiate between the environment of adsorbed species was used to study the adsorption of materials onto activated carbon over long time periods. Figure 3 shows the ^{31}P NMR spectrum for TMP adsorbed onto SC2 carbon at time zero (solid line) and time ~20 hours (dotted line).

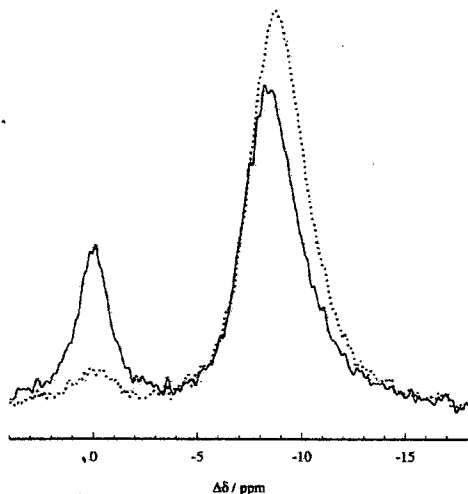


Figure 3: Time interval NMR spectra of TMP adsorbed onto SC2 carbon

The data in figure 3 show that over the time period of the experiment, TMP gradually filled the most shielded pores with loss of "free" adsorbate from less

restricted parts of the system. Many other experiments of this type have been carried out to study the dynamics of the adsorption process. Competitive adsorption was also studied. Figure 4 shows typical data; TMP (solid symbols) is shown to be displaced from the pores of SC2 carbon by the addition of dimethyl methylphosphonate (DMMP - open symbols) over a 16 hour period.

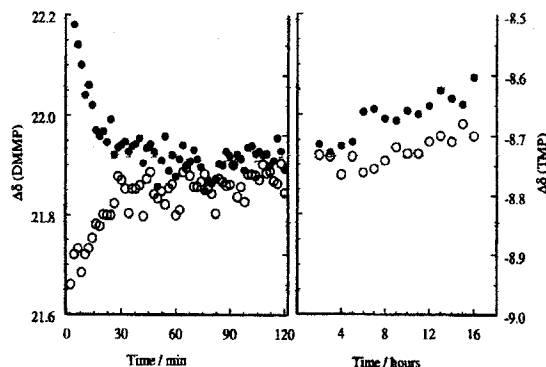


Figure 4: Competitive adsorption between TMP and DMMP

Conclusions

MAS-NMR has been shown to be a powerful experimental technique for studying dynamic processes occurring during the adsorption of materials onto activated carbon

References

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