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Advanced NMR-Based Techniques for Pore Structure Analysis of Coal

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Background

One of the main problems in coal utilization is the inability to properly characterize its complex pore structure. Coals typically have micro/ultra-micro pores but they also exhibit meso and macroporosity. Conventional pore size techniques (adsorption/condensation, mercury porosimetry) are limited because of this broad pore size range, microporosity, reactive nature of coal, samples must be completely dried, and network/percolation effects. Small angle scattering is limited because it probes both open and closed pores. Although one would not expect any single technique to provide a satisfactory description of a coal's structure, it is apparent that better techniques are necessary. We believe that measurement of the NMR parameters of various gas phase and adsorbed phase NMR active probes can provide the resolution to this problem. We will investigate the dependence of the common NMR parameters such as chemical shifts and relaxation times of several different nuclei and compounds on the pore structure of model microporous solids, carbons, and coals. In particular, we will study the interaction between several small molecules (^{129}Xe , ^3He , $^2\text{H}_2$, $^{14}\text{N}_2$, $^{14}\text{NH}_3$, $^{15}\text{N}_2$, $^{13}\text{CH}_4$, $^{13}\text{CO}_2$) and the pore surfaces in coals. These molecules have been selected for their chemical and physical properties. A special NMR probe will be constructed which will allow the concurrent measurement of NMR properties and adsorption uptake at a variety of temperatures. All samples will be subjected to a suite of "conventional" pore structure analyses. These include nitrogen adsorption at 77 K with BET analysis, CO_2 and CH_4 adsorption at 273 K with D-R (Dubinin-Radushkevich) analysis, helium pycnometry, and small angle X-ray scattering as well as gas diffusion measurements. The project combines expertise at the UNM (pore structure, NMR), Los Alamos National Laboratory (NMR), and Air Products (porous materials).

Work completed during the last quarter

We now have two suites of well-characterized microporous materials including oxides (zeolites and silica gel) and activated carbons from our industrial partner, Air Products in Allentown, PA. Our current work may be divided into three areas: small-angle X-ray scattering (SAXS), adsorption, and NMR.

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1. SAXS.

We have started SAXS-contrast matching experiments. For these, we use an adsorbate which has the same electron density as the solid. Therefore, we observe scattering from the adsorbate-vapor interface instead of the solid-vapor interface (if no adsorbate) or a complex combination of the solid-adsorbate and adsorbate-vapor interfaces if an adsorbate is used with different electron density. This type of experiment should enable a new level of pore structure information to be obtained from SAXS. However, experimental difficulties as well as academic problems of the graduate student associated with this part of the project have resulted in no new results for the quarter. Both problems should be rectified during the next quarter.

2. Adsorption.

Prior to analysis by NMR, high pressure gas sorption was carried out on a set of seven activated carbons supplied by Air Products. Methane adsorption at ~ 22 $^{\circ}\text{C}$ and carbon dioxide adsorption at 0 $^{\circ}\text{C}$ was measured over a range of equilibrium pressures (0- 400 psia). A number of analyses were carried out using this data and the results obtained were correlated with data obtained from Small Angle X-ray Scattering (SAXS), molecular probe size exclusion studies, and carbon tetrachloride activity data. Adsorption isotherms for methane and carbon dioxide are presented in Figures 1 and 2. All carbons exhibited Type 1 isotherms for both methane and carbon dioxide indicating the presence of microporosity. The degree of microporosity can be estimated qualitatively by the steepness of the lower-pressure leg of the isotherm, and by the flatness of the plateau at the higher pressure end. As expected, CO_2 uptakes were higher than methane uptakes at the same relative pressure. Carbon dioxide is below its critical temperature at this adsorption temperature unlike methane which is far above its critical point at room temperature. Consequently, CO_2 molecules have a greater affinity for adsorption than methane molecules. Also possibly affecting uptake is the shapes of the two adsorptive molecules; methane is almost spherical whereas CO_2 is linear and so, may be more accessible to the slit-shaped pores in carbon.

The surface areas of the carbons were estimated from the isotherms using the Dubinin-Radushkevich (DR) equation. This equation is widely used for analyzing microporous adsorbents even though the concept of a surface area loses its significance when the pore sizes are of the same order of magnitude as that of the adsorbate. In this case the "surface area", while not corresponding to the geometric area of the surface, does provide an estimate of the adsorptive capacity of the adsorbent for a particular adsorbate. The methane DR plots showed significant deviations from linearity for the carbons with high methane uptakes. Marsh et al explained this kind of "positive deviation" as due to the presence of larger pores, i.e. the skewing of the pore size distribution due to larger pores being present and hence rendering the plot non-linear. DR plots are shown in Figures 3 and 4. For CO_2 , two of the carbons, -071.03 and -058.57, also show similar deviations but these are possibly due to the presence of constrictions, i.e., pores whose "mouths" are narrower than the rest of the pore and hence they start to get filled only at higher

pressures when molecules can push their way in through the narrow openings. Further studies will be carried out to confirm this hypothesis by studying adsorption kinetics at different temperatures.

The DR surface areas obtained correlated well with the average radius of gyration as obtained from SAXS (see Table 1). For a greater degree of activation, more open pores are present and so one would expect increased adsorptive capacity for higher pressures while for smaller pores pore filling should attain completion at lower pressures. Thus, while smaller pores would mean an increased uptake at low relative pressures, the adsorptive capacity would increase with increase in activation. This is indeed the case. It was observed that samples with larger SAXS radius of gyration exhibited higher uptakes and higher DR surface areas. A comparison between DR surface areas determined from methane and carbon dioxide is given in Table 2. This comparison is interesting because the use of methane at this temperature is problematic. However, the surface areas seem to agree reasonably well given the uncertainties in molecular size for both adsorbates, in the extrapolated value of P_0 for methane, and accessibility concerns.

According to Dubinin and co-workers, the adsorption potential distribution function may be assumed to fit a Gaussian curve. Other mathematical functions have also been proposed for the distribution. Dubinin and Astakhov modified the DR equation and introduced another variable, the exponent, which quantifies the breadth of the distribution. Assuming that pore potential and pore size are related, the exponent in the Dubinin-Astakhov (DA) equation allows a semi-quantitative estimate of the pore size distribution breadth. The DA exponent was calculated for each of the carbons using both methane and carbon dioxide and a trend was noticed in the variation of the exponent with the DR surface area. The DA exponent is expected to vary between numerical values of 1 and 3. Values close to 1 indicate a wide pore size distribution whereas values closer to 3 would point toward a narrow distribution of pore sizes. The DR equation is thus a special case of the DA equation with its exponent as 2. One could surmise that for microporous carbons such as these a wider distribution would indicate the presence of more open pores due to increased activation. The first pores to be formed on activation are ultramicropores and as further activation is carried out, the pores widen out and become more open. Of course new small pores will also be formed but this will not compensate for the effect of widening of the pores already present. An increase in surface area for methane, and average SAXS radius of gyration is accompanied by a lowering of the DA exponent, indicating the presence of more porosity. For CO_2 , several of the carbons show seemingly unexplainable low values of the DA exponent. This could be the result of two effects. The adsorption isotherms and therefore $\text{Log}(P_0/P)^2$ has a limited range. Therefore, all adsorption results must be considered to be preliminary until subambient adsorption measurements are made during the next quarter. Another possible cause is the question of molecular accessibility previously discussed. This will be addressed by varying equilibration time as a function of adsorption temperature.

Studies were carried out at Air Products using a range of molecule probes of different sizes. The extent of adsorption by various molecules at high relative pressure ($P/P_0 \sim 0.5$) gives us an idea of the sizes of the pores present for microporous solids. Results are summarized in Table 3. These measurements are related to the carbon tetrachloride activity, expressed as wt.% CCl_4 /wt. carbon, values reported in Table 1. The molecule, with a diameter of 6 Å will adsorb less if there are smaller pores from which it is excluded. Samples with greater CCl_4 activity, have been activated to a greater degree and should exhibit higher surface areas.

TABLE 1
Comparison of preliminary results obtained from high pressure
methane adsorption with SAXS and CCl_4 activity.

Sample ID, 7461-	SAXS r_g Å	DR SA, m^2/g	CCl_4 activity, %	DA exponent
071.03	6.0	738	30	1.98
028.16	6.3	1841	not microporous	1.66
071.18	6.8	1337	113	1.24
071.19	6.2	1167	81	1.53
071.20	6.1	860	60	1.85
071.21	6.6	1302	102	1.63
058.57	5.0	342	<10	2.45

TABLE 2
Comparison of preliminary results obtained from high pressure
methane and carbon dioxide adsorption

Sample ID, 7461-	DR SA CH_4 (m^2/g)	DR SA CO_2 (m^2/g)	DA exp. CH_4	DA exp. CO_2
071.03	738	758	1.98	1.31
028.16	1841	2650	1.66	1.34
071.18	1337	1628	1.24	1.59
071.19	1167	1270	1.53	1.81
071.20	860	1001	1.85	2.04
071.21	1302	1517	1.63	1.59
058.57	342	473	2.45	1.00

TABLE 3
Molecular probe size exclusion results
(Uptakes in cm^3/g)

Sample/ molecule size	CCl ₄ , 6.0 Å	i-C ₅ H ₁₂ , 4.9 Å	CHCl ₃ , 4.6 Å	nC ₄ H ₁₂ , 4.3 Å	CH ₂ Cl ₂ , 4.0 Å	CS ₂ , 3.7 Å
7461-						
058.57	0.003	0.018	0.029	0.052	0.146	0.171
071.18	0.754	0.777	0.729	NA	NA	NA
071.20	0.406	0.419	0.404	NA	NA	NA

3. NMR Techniques.

Recent progress will be separated into hardware development and implementation and actual NMR data. In the former category, we have just completed the development and testing of a NMR probe system and cryostat that gives us the capability of NMR experiments at temperatures from about 3 to 400 K. The probe system has been tested over the NMR frequency range needed for most of the compounds of interest. The sample size is essentially a cylinder of about 14 mm diameter and 16 mm length. The probe system includes a capillary tube connected to a gas handling system. This allows us to monitor and change the pressure of the gas over the sample. The pressures available are $\sim 10^{-5}$ torr to ~ 5 atmospheres. At the highest pressure, the failure comes by leakage of an o-ring seal rather than catastrophic failure. It is our belief that this entire system will allow the greatest flexibility in testing adsorption, monitoring adsorption properties, and performing *in situ* NMR using almost any NMR active gas and any porous material.

To establish the computer analysis methodology and to obtain a "baseline" on NMR capabilities, we have been duplicating some of the pore size measurements that have been published in the literature. These were done with existing, commercial NMR probes and special sample tubes. Work was concentrated on duplicating ¹²⁹Xe measurements of pore sizes in zeolites. We were successful in duplicating several published experiments on zeolite-Y and mordenite and extending the studies to lower Xe pressures than has been reported. Our experience is that the published literature does not faithfully describe features in the spectra that are a bit problematical. In fact, we observe a broad ¹²⁹Xe NMR peak in virtually all zeolite samples that is not mentioned in the literature and which we attribute to adsorption on poorly characterized amorphous material in the sample. We also find that the ¹²⁹Xe NMR spectra are unusually sensitive to the details of the sample preparation. For example, we routinely heat the sample in a "shallow bed" configuration at about 675 K for 4 to 8 hours before adding Xe to NMR. We find that the shifts and the amount of "amorphous signal" will change slightly if we heat for 24 hours

instead of 8. This result is not terribly surprising since the ^{129}Xe NMR measurement is actually a measure of the interaction of Xe with the surface of the material. However, we would prefer a pore size measurement technique that is much less sensitive to the details of the preparation. We have also checked our new probe system with our older data and find the agreement nearly perfect when using ^{129}Xe pore measurement techniques. Finally, because of the better sensitivity of the new probe system, we have attempted ^{131}Xe NMR of xenon adsorbed in zeolite-Y. We have obtained a signal but the linewidth is extremely broad. This quick experiment was performed because the nuclear electric quadrupole moment of ^{131}Xe is a property that may well be exploited for investigating pore sizes.

Work planned for next quarter

Our goals for the next quarter include:

1. Low pressure adsorption studies using automated adsorption systems for these carbons. Comparisons between the low and high pressure isotherms for methane and carbon dioxide will permit conclusions to be drawn based on the differences in the adsorption of the two gases. The presence of constricted pores possibly indicated in two samples will be probed by adsorbing CO_2 at another temperature. With the complete isotherms, attempts will be made to obtain a more rigorous and quantitative estimation of the heterogeneity in these adsorbents, using different mathematical models, and different forms for the distribution function.
2. Continue contrast-matching SAXS experiments on CPG phase-separated glasses and start contrast-matching SAXS experiments on carbon samples.
3. Start $^{14}\text{N}_2$ and $^{15}\text{N}_2$ NMR experiments of nitrogen adsorbed in zeolites to duplicate the conditions of BET experiments.

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Fig. 1 Methane adsorption on carbons

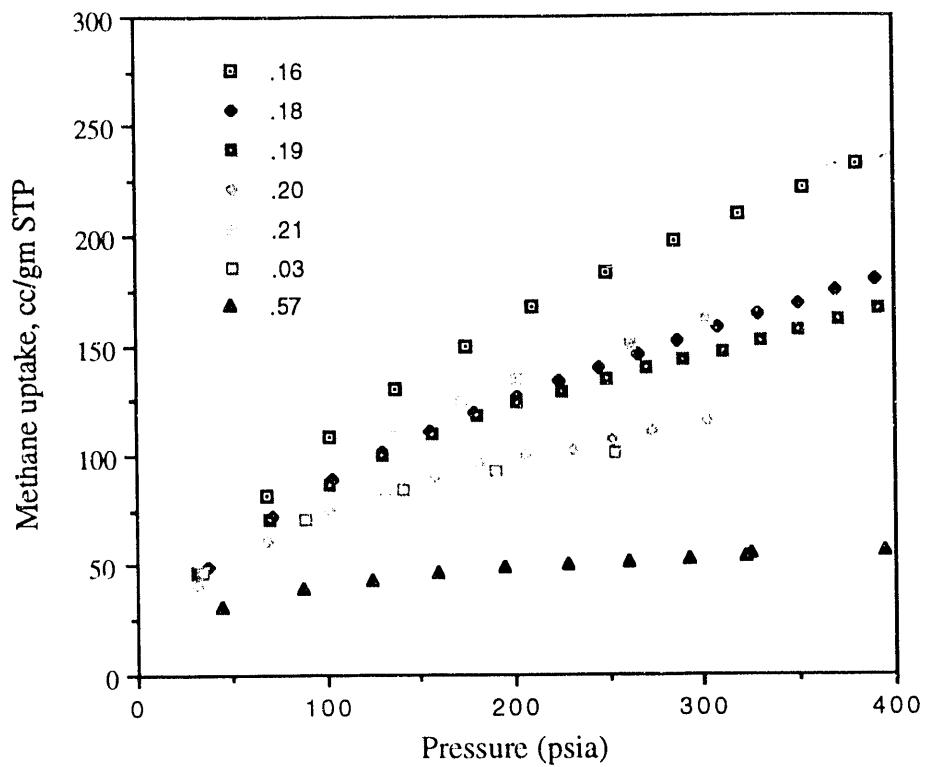


Fig. 2 CO₂ uptakes on carbons

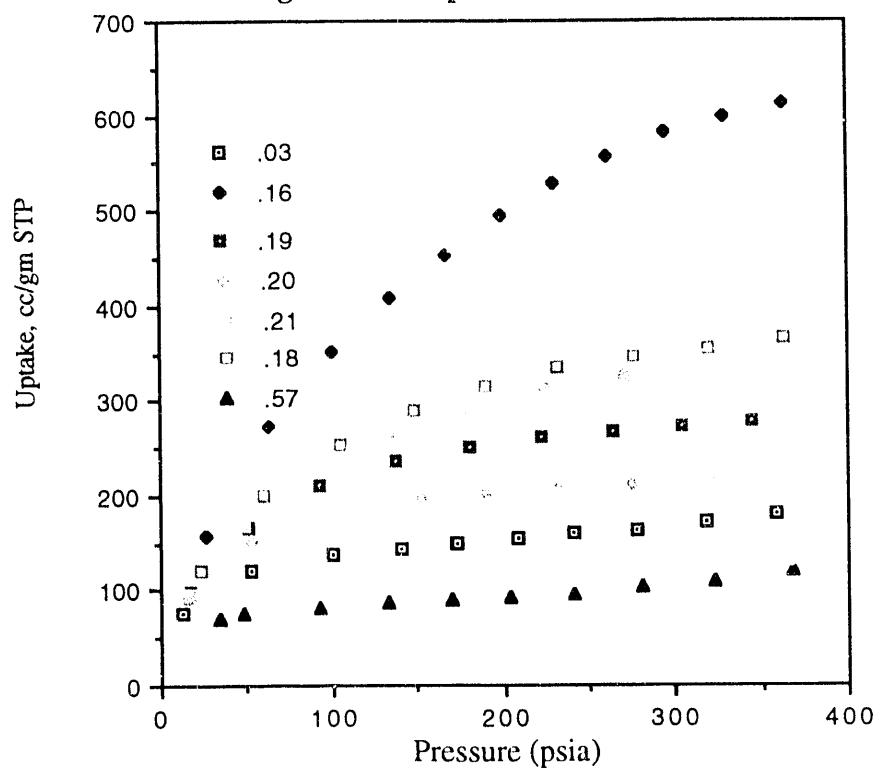


Fig. 3 DR plots for methane on carbon

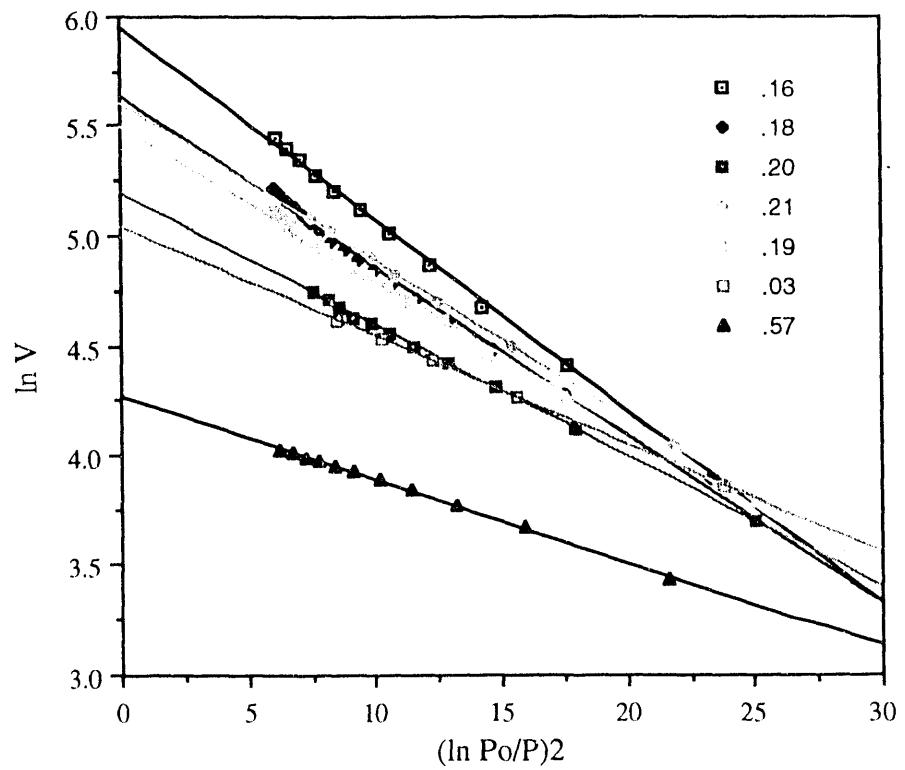
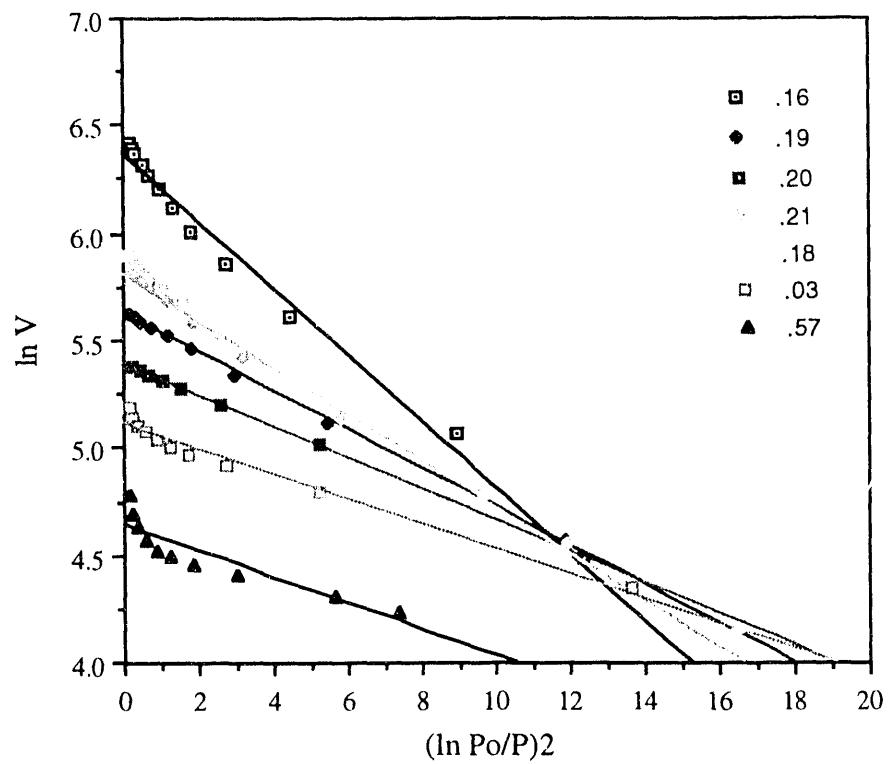


Fig 4. DR plots for CO₂ on carbon



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