HYDROGEN STORAGE ON ACTIVATED CARBON

Final Report

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ABSTRACT

The project studied factors that influence the ability of carbon to store hydrogen and developed techniques to enhance that ability in naturally occurring and factory-produced commercial carbon materials. During testing of enhanced materials, levels of hydrogen storage were achieved that compare well with conventional forms of energy storage, including lead-acid batteries, gasoline, and diesel fuel. Using the best materials, an electric car with a modern fuel cell to convert the hydrogen directly to electricity would have a range of over 1,000 miles. This assumes that the total allowable weight of the fuel cell and carbon/hydrogen storage system is no greater than the present weight of batteries in an existing electric vehicle. By comparison, gasoline cars generally are limited to about a 450-mile range, and battery-electric cars to 40 to 60 miles.

The project also developed a new class of carbon materials, based on polymers and other organic compounds, in which the best hydrogen-storing factors discovered earlier were "molecularly engineered" into the new materials. It is believed that these new molecularly engineered materials are likely to exceed the performance of the naturally occurring and manufactured carbons seen earlier with respect to hydrogen storage.

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EXECUTIVE SUMMARY

The interrelationship between the source material for activated carbons, its structure, and surface chemical effects during hydrogen adsorption has been studied. The objective of the proposed research continues to be to establish this relationship and to then develop chemical pre-treatment procedures and synthesis strategies that will significantly improve hydrogen adsorption capacity on existing and new carbons. The results from this comprehensive program will permit manufacturing specifications to be precisely tuned for optimal performance of activated carbons as hydrogen storage media and will provide the basis for optimization of next-generation materials.

A battery of experimental techniques has been employed. Phase I called for adsorption isotherms up to pressures of 1000 psi to be obtained on carbons derived from different source materials. Isosteric heats and surface energy heterogeneity were determined from these data. Nitrogen adsorption was used to evaluate carbon microstructure. Results clearly indicate that microstructure and surface chemistry both affect hydrogen adsorption. During Phase II, both the microstructure and surface chemical functionality was modified by controlled oxidation and their combined effects "tracked" by the use of hydrogen as a probe adsorbate. What is desired is an activated carbon whose adsorption/storage meets current demands for vehicle application as well as an understanding why the material meets the requirements.

Success in this comprehensive program has precedence. Professor Schwarz's laboratory has been actively involved in developing novel storage facilities for alternative fuel gases since 1982. Under contract to Brookhaven National Laboratories, an economical system was developed that met Department of Energy performance criteria. These accomplishments have led to two U.S. patents and a pending patent, world-wide acknowledgement in the March 8, 1989 and February 12, 1993 issues of *The Wall Street Journal*; and the establishment of a Syracuse University Laboratory for the Study of Storage Systems for Hydrogen (LASSH). Currently, three post-doctoral researchers and one Ph.D. student are actively involved in research to develop novel carbon-based storage media for mobile and stationary application. The expertise of the Syracuse

Laboratory and the additional resources provided by Brookhaven National Laboratories insure development of practical hydrogen storage facilities.

This assertion is supported by laboratory data obtained during the contract period for existing carbons which demonstrate that a gravimetric density of 1.45 kwh/kg and a volumetric density of 664 Wh/l is feasible. These figures are based on entire storage systems weight including carbon, hydrogen, and vacuum jacketed insulated composite container. The actual amount of hydrogen stored is 2.95 kg. This amount of hydrogen will suffice for vehicular applications since approximately 3.3 kg of hydrogen is needed for a 200 km driving range for a compact hydrogen internal combustion engine powered car, and a greater driving range is expected in the case of a PEM fuel cell powered vehicle. Furthermore, discharge rate experiments demonstrate that activated carbon can release hydrogen at high rates without additional heating. Therefore, carbon storage will satisfy the demands of either PEM fuel cells or internal combustion engines for vehicles.

A new class of activated carbons molecularly engineered (ACME) adsorbents for hydrogen storage has also been developed during this contract period. ACME samples have been synthesized in "molecular containers" that offer a wide range of "container" dimensions. The activated carbon precursors are organic compounds (polymers, carboxylic acids) whose oxygen content can be precisely controlled. ACME samples have been screened for their hydrogen storage capacity using our research. These new generation materials are highly microporous and are likely to supersede the performance of materials that are currently commercially available.

INTRODUCTION

Activated carbon means carbonaceous materials with a large adsorption capacity. Activated carbons can be manufactured from many different raw materials such as coconut shells, wood, peat, and coal. One might expect that the carbon's performance as an adsorbent in a particular application will depend on its source. Indeed, we find that this is the case. The demands placed on activated carbon-based technologies have outpaced fundamental studies of the interplay between the carbon's source, the surface chemical properties of carbons, the **accessible** internal adsorption area, and their

performance as adsorbents. Unfortunately, preconceived notions have been established which attempt to *a priori* provide "prescriptions" for carbon selection in a technological application. One focus of this proposed research is to apply a battery of techniques on classes of carbons so carbon selection criteria are scientific. The central objectives of this research effort are: 1) Determine the interrelationship between carbon source, activated carbon microporosity, surface chemical functionality, and hydrogen adsorption. 2) Develop chemical pretreatment procedures that will significantly improve hydrogen adsorption capacity of existing carbons. The techniques to be used and the methodology for analyzing the data they provide and the materials to be studied are conveniently divided into three areas: existing carbons, carbons synthesized in clays, and carbons synthesized in hydrotalcites.

EXISTING CARBONS

The adsorption characteristics of activated carbon are affected by the type of carbon, and that is governed by the source of raw material and the preparation procedures used during carbonization and activation (Huang, 1978). Any assessment of the adsorptive behavior of activated carbons based only on surface area is incomplete; carbons with equal density and equal surface area can exhibit different adsorptive characteristics when prepared by different methods. Some adsorptive properties can be explained by differences in pore size distribution. Surface chemical functionalities, derived from activation procedures, also influence adsorption, but their role depends on their accessibility, which, in turn, depends on the carbons microporosity. To demonstrate, activated carbons from different sources were obtained. Table 1 collects some of the important properties of the four carbons as specified by the manufacturer. The adsorption properties of these samples were studied at Syracuse University. Hydrogen isotherms at 78K for each carbon are presented in Figure 1. The data on Calgon show that it has the smallest adsorption capacity, while hydrogen storage on Norit exceeds 8% by weight of carbon at pressures less than 40 atm.

Figure 1

Adsorption Isotherms for H_2 on As-Received Carbons Determined at 77K

TABLE 1 - Selected Properties of Activated Carbons

Manufacturer	Carbon Source	BET Surface Area m^2/g	Density g/cc	Cost \$/lb Basis ~ 2000 lbs
North American Inc.	Coconut	1100	0.51	1.90
American Norit Inc.	Peat Moss	1000	0.49	1.74
Westvaco Inc.	Wood	1400-1500	0.265	1.46

Nitrogen adsorption data were collected at 78K, and these isotherms (Figure 2) were analyzed to obtain pore size distributions for each carbon by standard procedures assuming uniform cylindrical pores (Gregg et al., 1982). The results demonstrated that a majority of the pore volume was contained in pores whose radii were $< 20 \text{ \AA}$ (Figure

Figure 2
Nitrogen Adsorption Isotherms at 77K as Selected Carbons

Figure 3
Cumulative Pore Volume as a Function of Pore Radius
Determined from N_2 Data Shown in Fig. 2

3). This was expected, due to the high surface areas of each sample. These N_2 data can be examined further. The total surface area contained in pores greater than the "cut-off" limit of the Kelvin equation ($\sim 15\text{-}16\text{\AA}$) for the wood-based carbon was approximately 5 times greater than that of the peat-based carbon. Considering the total BET area of each carbon, this translates to about 70% of the adsorption space for hydrogen was in the micropores of the wood-based carbon, whereas more than 90% of the adsorption space was in the micropores of the peat-based carbon.

The complex topographies associated with carbon microporosity can also be described in terms of fractal geometry. Recently, an isotherm equation for adsorption on fractal surfaces was proposed (Avnir and Jaroniec, 1989). When the N_2 adsorption data are analyzed to determine D , the fractal dimension of the surface accessible to adsorption, we find $D_{\text{peat}} > D_{\text{wood}}$. This result is consistent with that presented above and provides a convenient *index* for characterizing carbon microporosity.

We concluded that hydrogen adsorption capacity on this set of carbons could also be controlled by factors other than those related to structure. Specifically, we cited that carbon surface chemistry plays an important role in storage capacity.

We initiated a study in which a hierarchy of treatment procedures was used to modify the surface functionalities on each of these carbons. Both microstructural and surface chemical characterization of the untreated and treated carbons have been obtained in addition to the effect of treatment on hydrogen adsorption storage. To this end, data have been obtained on the carbon derived from peat moss (Norit), and the procedures and results are described below.

The Norit carbon was treated as follows.

About 500 ml concentrated nitric acid (15.8 N) was used to treat 35 g of activated carbon. The carbon was added slowly at room temperature to the solution of concentrated nitric acid. Mechanical stirring was provided during addition. A vigorous exothermic reaction with the evolution of brown fumes (NO_2) took place. The mixture reached a final temperature of about 45°C , and stirring was continued for 3 h. After treatment, the carbon was separated by decantation and washed several times with

distilled water. The product was then placed in a Soxhlet extractor and washed further with hot distilled water until a constant pH of water was obtained.

Nitrogen adsorption data were obtained to assess the impact of the above treatment procedures on the microstructure of the carbon. About 100 mg of carbon were placed in a Cahn RG2 recording electrobalance. The adsorption experiments were carried out at liquid nitrogen temperature. The carbon was slowly outgassed at 453K to a residual pressure of 2 Pa for 12 h. The system was then slowly cooled to ambient temperature. After further cooling to 78K, ultrahigh purity N_2 was introduced in small increments, and the pressure was recorded by MKS Baratrons (222AHS, 222BA, 310BHS-1).

The apparent surface area and total cumulative pore volume was obtained based on the measured isotherms. Changes in the surface chemical functionalities of the carbon due to treatment were determined by the Boehm titration. Here, the strength and number of acidic groups are found by titration with NaOH, Na_2CO_3 , and $NaHCO_3$. The basic groups of all strengths are found by titration with HCl.

Hydrogen adsorption isotherms were measured at two temperatures. We found that there was a significant increase in storage capacity due to the nitric acid treatment and the maximum storage can be achieved at a much lower pressure than is required for comparable storage on the untreated carbon samples. The results are collected below:

- 1) Table 2 presents the microstructural data for the treated and untreated carbons. They show that treatment changes the carbon surface area and total cumulative pore volume minimally. In fact, the data would suggest that the treated carbon should have a lower adsorption capacity because both its surface area and pore volume decrease when compared to the untreated carbon.
- 2) Table 3 presents the results from the Boehm titration. There is a significant increase in the acidic character of the treated carbon.
- 3) The hydrogen isotherms at 78K are shown in Figure 4 for the untreated and treated Norit carbon. The amount of hydrogen adsorbed increases rapidly and becomes essentially constant at a pressure of ~ 5 atm. The untreated carbon data

show that pressures > 35 atm are required to store a comparable amount of hydrogen.

Figure 4
Effect of Oxidation on Adsorption of H_2 (77K)

Impact

Pressure is an important design variable in hydrogen adsorption/storage systems. The critical parameter is the weight of hydrogen based on total system weight. Lowering the pressure relaxes the weight required for safe containment vessels thus increasing the weight-% of hydrogen.

TABLE 2 - Structural Properties

	Surface Area (m ² /g)	Total Cumulative Pore Volume (ml/g)
Norit untreated	1267.0	0.94
Norit treated	1128.5	0.92

TABLE 3 - Boehm Titration Results

Sample	Amount of HCl [meg/100g]	Amount of NaHCO ₃ [meg/100g]	Amount of Na ₂ CO ₃ [meg/100g]	Amount of NaOH [meg/100g]
Norit	68.25	2.50	10.00	23.75
Norit OX	27.00	29.00	34.00	75.00

Recently, other carbons were examined for their hydrogen storage capacity. We found them to be exceptional, exhibiting the following properties:

MICROSORB, at T = 78K, P = 39 ATM

Amount of hydrogen stored is 11.2% by weight and 29.2 kg/m³ on a volume basis (356.86 v/v at STP).

SUPERACTIVATED, at T = 78K, P = 36 ATM

Amount of hydrogen stored is 11.2% by weight and 24.2 kg/m³ on a volume basis (296.49 v/v at STP).

MOLECULARLY ENGINEERED CARBONS

Existing materials, while convenient, restrict developing the next generation of needed properties in adsorbents. Design principles whereby the structural and chemical properties of suitable precursors are exploited to create new materials can be designated

molecular engineering. This conceptual idea has seen repeated applications in recent years. For example, in microelectronics the biochip offers the potential of constructing, by building up from individual molecules, electronic devices, thus offering alternatives to the silicon-based technological strategy of shrinking large structures to meet the demands of very large scale integration.

Microporous materials, such as activated carbons and zeolites have many applications in the industrial sector. They can be used as catalyst carriers, as catalysts themselves, molecular sieves, and sorbents. Unfortunately, their design and construction protocol is poorly understood in relation to their end use. The molecular engineering of such materials is an attractive approach, and one of the objectives of our research is to provide a molecular engineering strategy. The next two sections describe novel classes of materials which we will use in our research plan.

Carbons Synthesized in Clays

Over the past 15 years, there has been a renewed and growing interest in the use of layered materials for specific technological applications. The intercalation of layered smectites (clays) with hydroxy-metal polycations is a method of mineral modification developed in the late 1970's (Brindlay & Sempels, 1977; Brindlay and Yamanaka, 1979). The method involves the introduction of large metal polycations into the interlayer spaces of clay minerals using ion exchange from aqueous solutions. The polycations act as "pillars" supporting the layers and, in addition, make the structure rigid after calcination. After heat treatment, the hydroxycation "pillars" are converted into oxide "pillars" (Occelli and Tindwa, 1983). The intercalated smectite is characterized by large specific surface area, developed porous structure and high surface acidity (Lahav et al., 1978; Vaughan et al., 1979; Occelli and Tindwa, 1983; Brindlay and Yamanaka, 1979).

Based on the idea of Pekala and Hopper (1987), Sonobe et al. (1990) prepared microporous carbon using the sodium form of montmorillonite as a matrix. This form of mineral has a very small interlayer distance (about 1.24 nm). After imbibition and processing furfuryl alcohol and polyvinyl acetate, they obtained a homogeneous carbon with a spacing 0.337 nm.

The properties of smectites depend on the manner of modification of the initial mineral and on the heat treatment of the resulting product. As an extension of the earlier work of Sonobe et al. (1990), we used the intercalated form of smectite modified in different ways as a starting matrix to obtain microporous carbon in the interlayer spaces of the clay mineral. The interlayer spacing of smectite intercalated by hydroxy-aluminum oligocations is quite different from the sodium form of this mineral; it has a value of 1.92 nm with a microporous volume of about 90 mm³/g and surface area of 400 m²/g (Brindlay and Yamanaka, 1979; Zyla and Bandosz, 1987). By saturating this material with furfuryl alcohol followed by polymerization and then carbonization of the interlayer compound we have obtained new adsorbents whose chemical and physical properties can be conveniently manipulated to provide tailored micro-structures for adsorption/storage applications.

Carbons Synthesized in Hydrotalcites

Another strategy in the preparation of activated carbons molecularly engineered as adsorbents for gas storage is to synthesize materials with well-defined structure and composition that can be repeatedly reproduced. The main difficulties in utilization of natural smectites for this purpose are that the composition and characteristics of natural smectite deviate from source to source, and they are usually contaminated with other mineral forms.

Synthetic hydrotalcite-like structures (HTLs) are attractive candidates for our studies. Their smectite-like size and layered framework, ion-exchange properties, and varied structural porosity allow for controlled variance in the introduction of organic precursors between layers. Utilization of hydrotalcite-like structures in polymerization (Geismar et al., 1991; Laycock et al., 1991), and a route for synthesis of pillared hydrotalcites with thermal stability above 500°C have been developed (Drezdson, 1988, and 1990; Twu and Dutta, 1991).

The structure of natural hydrotalcite, $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}] \text{CO}_3 \cdot 4\text{H}_2\text{O}$, is derived from brucite, $\text{Mg}(\text{OH})_2$, by isomorphous replacement of octahedrally-coordinated Mg^{2+} cations with Al^{3+} cations. The resulting positive charge on the metal hydroxide layers is balanced

by exchangeable carbonate anions in the interlayer region of the structure. Synthetic hydrotalcite-like structures (HTLs) can be prepared with a wide variety of divalent and trivalent cations and their ratios. Thus, HTLs can be described by the general formula:

where $M(II) = Mg, Zn, Ni, Co, \dots$, $M(III) = Al, Fe, Cr, Mn, \dots$, $A^{n-} = OH^-, CO_3^{2-}, Cl^-, NO_3^-$, $Mo_7O_{24}^{6-}$, $V_{10}O_{28}^{6-}$, $V_{10}O_{28}^{6-}$, $[Fe(CN)_6]^{2(3)-}$, organic anions..., (Miyata, 1975; Drits, 1987; Drezdson, 1990; Sato, 1991) (Fig. 5).

Figure 5
Schematic of Hydrotalcite Structure

The layers in HTLs can be stacked with two layers per unit cell in hexagonal symmetry (manasseite; $P6/mmc$ space group), or with three layers per unit cell in rhombohedral symmetry (hydrotalcite; $R3m$ space group). The two forms are very similar in their physical properties and are therefore nearly indistinguishable without the help of x-rays.

The interlayer space in the hydrotalcite-like structures provides a reactive environment. The weakness of bonding between layers allows for introduction of different anions and formation of intercalation compounds with organic and organometallic, silicate, and polyoxometalate compounds. Polyoxometalate ions introduced into the HTLs as pillars increase the thermal stability of these materials and after calcination display high values of surface area. Table 4 reports some examples of pillared polyanions and organic compounds intercalated into the HTLs.

TABLE 4 - HTLs Exchanged with Pillaring Anions

Organic Anions	Polyoxometalates
terephthalate	$[\text{Mo}_7\text{O}_{24}]^{6-}$
p-toluene-sulfonate	$[\text{V}_{10}\text{O}_{28}]^{6-}$
dihydroxy-benzene-disulfonate	$[\text{PMo}_6\text{V}_6\text{O}_{40}]^{5-}$
naphtalene-disulfonate	$[\text{PMo}_6\text{W}_6\text{O}_{40}]^{3-}$
styrene-sulfonate	$[\text{PMo}_{12}\text{O}_{40}]^{3-}$
polystyrene-sulfonate	$[\text{Ta}_6\text{O}_{18}(\text{OH})]^{7-}$ $[\text{Nb}_6\text{O}_{18}(\text{OH})]^{7-}$ $[\text{PW}_{12}\text{O}_{40}]^{3-}$ $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{5-}$

The x-value for single-phase synthetic HTLs compounds is generally reported to be $0.2 < x < 0.33$ (Miyata, 1980), although by using hydrothermal syntheses the upper range can be extended to $x = 0.44$.

Currently, we are exploring the effect of a constant spacing and varying net charge. By varying the charge, we vary the density of carbonaceous material between the sheets. When this material is converted to "activated carbon", the result is carbons with different pore structures. The pore structure is critical in determining the storage capacity of these materials.

A structure that is ideal for adsorption of one adsorbate (say H_2) might not (and is likely to) be efficient for storage of another adsorbate (say CH_4) from the point of view of size consideration.

This fact is emphasized in Figure 6 which shows a model for the adsorption capacity of H_2 and CH_4 on template carbon structures. If the adsorbate close-packs the theoretical adsorption capacities for either H_2 or CH_4 can be evaluated as shown in Figure 6. The practical limit is $n = 4$ because the structure would be unstable above this value.

MATRIX-CARBON SYSTEM

Monolayer hydrogen adsorption on the sheet

Adsorption capacity

H₂/Carbon

$\approx 26 \% \quad (\text{w/w})$

$\approx 2.2 \times 10^4 \text{ Y(STP)/Y}$

CH₄/Carbon

$\approx 17 \% \quad (\text{w/w})$

$\approx 1.5 \times 10^3 \text{ Y(STP)/Y}$

Multilayer hydrogen adsorption between the sheets

Adsorption capacity

H₂/Carbon

$\approx n/2 * 26 \% \quad (\text{w/w})$

$\approx (n/2) * 2.2 \times 10^4 \text{ Y(STP)/Y}$

CH₄/Carbon

$\approx n/2 * 17 \% \quad (\text{w/w})$

$\approx (n/2) * 1.5 \times 10^3 \text{ Y(STP)/Y}$

Figure 6
Schematic Model of Gas Adsorption on Engineered Carbons

Our work on the template carbon structure derived from either smectites or hydrotalcites has received considerable interest from the scientific community. We find these materials are microporous, and their microporosity can be "tuned" to accommodate specific adsorbates. Appendix I contains abstracts from recent publications that deal with the structural and adsorption properties of those molecularly engineered materials (Papers 7,8,12,13, and 17).

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6. Jagiello, J., Bandosz, T.J., and Schwarz, J.A. (1991), "Application of Inverse Gas Chromatography at Infinite Dilution to Study the Effects of Oxidation of Activated Carbons", *Carbon*, 30(1), 63-69.
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9. Jagiello, J., and Schwarz, J.A. (1992), "Energetic and Structural Heterogeneity of Activated Carbons Determined Using Dubinin Isotherms and an Adsorption Potential in Model Micropores", *J. of Colloid and Interf. Sci.*, 154(1), 225-237.

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11. Bandosz, T.J., Putyera, K., Jagiello, J., and Schwarz, J.A. (1993), "Application of Inverse Gas Chromatography to the Study of Surface Properties of Modified Layered Minerals", *Microporous Materials*, 1, 73-79.
12. Bandosz, T.J., Jagiello, J., and Schwarz, J.A. (1993), "Effect of Surface Chemical Groups on Energetic Heterogeneity of Activated Carbons", *Langmuir*, 9, 2518-2522.
13. Jagiello, J., and Schwarz, J.A. (1993), "Relationship Between Energetic and Structural Heterogeneity of Microporous Carbons Determined on the Basis of Adsorption Potentials in Model Micropores", *Langmuir*, 9, 2513-2517.
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16. Bandosz, T.J., Jagiello, J., Contescu, Cr., and Schwarz, J.A. (1993), "Characterization of the Surfaces of Activated Carbons in Terms of Their Acidity Constant Distributions", *Carbon*, 31(7), 1193-1202.
17. Bandosz, T.J., Putyera, K., Jagiello, J., and Schwarz, J.A., "A Study of Carbon-Smectite Composites and Carbons Obtained by In-Situ Carbonization of Polyfurfuryl Alcohol", *Carbon*, in press.

Recitals

1. "Hydrogen Storage on Activated Carbons", World Hydrogen Energy Conference, Honolulu, Hawaii, July 1990.
2. "Hydrogen: A Clean Fuel for the Future", New York City Department of Transportation, New York, NY, March 1991.
3. "The Future is a Gas", 2nd National Hydrogen Association Meeting, Washington, D.C., March 1991.

4. "Performance Evaluation of the Hydrogen Storage Process Development Unit", Inter-national Energy Association Task VII Workshop, Golden, CO, August 1991.
5. "Adsorption/Storage of Hydrogen Activated Carbons", 3rd Meeting of the National Hydrogen Association, Washington, D.C., March 1992.
6. "Isotope Effects During Hydrogen Adsorption in Activated Carbons", Kentucky Center for Applied Energy, Lexington, KY, May 1992, invited.
7. "The Carbon Liquid Interface", North American Carbon Conference, Atlanta, GA, May 1992, invited.

Patents

1. "Activated Carbons Molecularly Engineered", Filed, January 27, 1993.

APPENDIX I

Abstracts from Publications Related to ACME Samples

The local exact and approximate solutions of the adsorption integral equation are presented. The Langmuir-like adsorption isotherm is assumed as a kernel. The exact local solution is compared with Sips' method. The accuracy and resolution of truncated approximations are discussed. The influence of experimental temperature on calculated results is also considered. Lateral interactions are taken into account for the random topography model of the adsorption sites.

Jagiello, J., and Schwarz, J.A. (1991), "Local Exact and Approximate Solutions of the Adsorption Integral Equation with a Kernel of a Langmuir-Like Adsorption Isotherm", *J. of Colloid and Interf. Sci.*, 146(2), 415.

Effects of the oxidation with nitric acid of active carbons from different origins have been studied by inverse gas chromatography. It is shown that the oxidation of activated carbons with nitric acid increases their acidity considerably, and at the same time decreases their adsorption affinity for n-alkanes, which is manifested by the decrease of the dispersive component of surface energy, γ_s^D , and adsorption enthalpies of alkanes. A correlation has been established between the acidity of carbons measured by base titration and the energy of the specific interactions with π bonds of unsaturated hydrocarbons.

Jagiello, J., Bandosz, T.J., and Schwarz, J.A. (1991), "Application of Inverse Gas Chromatography at Infinite Dilution to Study the Effects of Oxidation of Activated Carbons", *Carbon*, 30(1), 63-69.

The effects of oxidation of activated carbons are studied by means of high-pressure methane adsorption. Decreases in amounts adsorbed and adsorption enthalpies after oxidation are observed. Thermodynamic analysis of adsorption isotherms using the virial-type thermal equation of adsorption is presented. The calculated adsorption energy distributions are shifted to lower adsorption energies for oxidized carbons. The mean

adsorption energies decrease, indicating that oxidized carbon surfaces have lower affinity for methane adsorption.

Jagiello, J., Sanghani, P., Bandosz, T.J., and Schwarz, J.A. (1992), "Thermodynamic Study of High-Pressure Adsorption of Methane on Activated Carbons: The Effect of Oxidation on Pore Structure and Adsorption Energy Heterogeneity", *Carbon*, 30(3), 507-512.

The effect of oxidation with nitric acid on activated carbons from different origins has been studied by inverse gas chromatography at infinite dilution, Boehm titration, and mass titration to determine the point of zero change (PZC) of carbons. The effect of oxidation is to generate acidic groups, and this becomes more pronounced as the temperature of oxidation is increased. We find that the Boehm titration results and the carbons' PZCs correlate with the severity of the oxidation treatment. These methods "study" the surface of carbons by its response to an aqueous environment. Inverse gas chromatography results show that increasing acidity is reflected by an increase in the specific interaction of π electrons in n-alkenes with acidic centers on the surface of carbons. This method probes the donor/acceptor nature of the carbon's surface and provides information complimentary to that supplied by the other methods.

Bandosz, T.J., Jagiello, J., and Schwarz, J.A. (1992), "A Comparison of Methods to Assess Surface Acidic Groups on Activated Carbons", *Anal. Chem.*, 64(8), 891-895.

Activated carbons derived from four different source materials were subjected to controlled oxidation by nitric acid, and their resulting microstructure and surface chemical groups were studied. Classical titration procedures indicated the acid/base character of the carbons and inverse gas chromatography was used to study other properties. We find that carboxylic groups are the primary acidic functionality added by oxidation and that these groups can be removed by high temperature treatment without altering the microstructural changes induced by oxidation. Nitric acid treatment of these carbons produces highly acidic carbonaceous materials, and in some cases modifies

microstructure. We conclude that inverse gas chromatography at infinite dilution, along with the procedures outlined, provides a convenient way to study the effects of surface modification procedures on the structure and surface chemical properties of porous adsorbents.

Jagiello, J., Bandosz, T.J., and Schwarz, J.A. (1992), "Inverse Gas Chromatographic Study of Activated Carbons: The Effect of Controlled Oxidation on Microstructure and Surface Chemical Functionality", *J. of Colloid and Interf. Sci.*, 151(2), 433-445.

Effects of the oxidation with nitric acid of active carbons from different origins have been studied by inverse gas chromatography. It is shown that the oxidation of activated carbons with nitric acid increases their acidity considerably, and at the same time decreases their adsorption affinity for n-alkanes, which is manifested by the decrease of the dispersive component of surface energy, γ_s^D , and adsorption enthalpies of alkanes. A correlation has been established between the acidity of carbons measured by base titration and the energy of the specific interactions with π bonds of unsaturated hydrocarbons.

Jagiello, J., Bandosz, T.J., and Schwarz, J.A. (1992), "Application of Inverse Gas Chromatography at Infinite Dilution to Study the Effects of Oxidation of Activated Carbons", *Carbon*, 30(1), 63-69.

Inverse gas chromatography at infinite dilution, employing alkanes and alkenes as probes, has been used to characterize the surface properties of a series of smectites of varying chemical composition. The results of this study show that the acidic centers and the interlayer distances have a great influence on the specific interaction of the smectite surface with π -bonds of alkenes. High values of the specific interaction parameter, ϵ_π , are caused by the existence of strong acidic centers that are connected with interlayer cations as well as with the chemical structure of the mineral sheets. On the other hand,

alkanes, whose interaction with the smectites is predominantly dispersive, are unaffected by changes in the clays' composition and/or structure.

Bandosz, T.J., Jagiello, J., Andersen, B., and Schwarz, J.A. (1992), "Inverse Gas Chromatography Study of Modified Smectite Surfaces", *Clay and Clay Minerals*, 40(3), 306-310.

Modification of clay minerals by exchange, intercalation, calcination and imbibition of organics followed by their polymerization and carbonization was studied. The surface properties of the clays were investigated by inverse gas chromatography at infinite dilution employing alkanes and alkenes as probes; the structural properties were measured directly by X-ray diffraction and inferred from the results of high pressure hydrogen adsorption. Calcination of pillared smectites prior to polymerization and carbonization of organic material in the interlayer space leads to a microporous "activated carbon" that demonstrates unique properties as an adsorbent for hydrogen, significantly different from clays that have not been calcined.

Bandosz, T.J., Jagiello, J., Amankwah, K.A.G., and Schwarz, J.A. (1992), "Chemical and Structural Properties of Clay Minerals Modified by Inorganic and Organic Material", *Clay Minerals, Journal of the European Clay Groups*, 27, 435-444.

Adsorption on microporous carbons is investigated in terms of their micropore structure and their adsorption energy heterogeneity. The pore size heterogeneity is proposed to be a controlling factor for the adsorption energy heterogeneity. The relationship between adsorption energy and pore sizes is based on the dependence of the molecule-pore interaction potential well depth as a function of the pore width. The adsorption integral equation is used to analyze data generated from the DR and DA isotherms using typical experimental conditions. It is observed that the adsorption systems described by these isotherms are strongly heterogeneous from the standpoint of their adsorption energetics which are categorized by asymmetrical energy distributions with a broadening toward high energies. It is also shown that these distributions correspond to relatively narrow

and symmetrical peaks characterizing the distribution of pore sizes. The strong asymmetrical relationship between adsorption energy and pore width magnifies the energetic heterogeneity even though pore size distributions show only modest dispersion. It is demonstrated that the Henry's law region appears as a natural consequence of the assumed model.

Jagiello, J., and Schwarz, J.A. (1992), "Energetic and Structural Heterogeneity of Activated Carbons Determined Using Dubinin Isotherms and an Adsorption Potential in Model Micropores", *J. of Colloid and Interf. Sci.*, 154(1), 225-237.

Surface properties of activated carbons and carbon fibers subjected to oxidation processes are investigated by means of inverse gas chromatography (IGC). A general correlation between surface density of acidic groups and the empirical parameter ϵ_{π} related to electron acceptor interactions is established. Model adsorbents based on benzene derivatives with known numbers of functional groups are also studied by IGC to examine the effect of surface geometry in relationship to the ϵ_{π} results from the carbons.

Jagiello, J., Bandosz, T.J., and Schwarz, J.A. (1992), "A Study of the Activity of Chemical Groups on Carbonaceous and Model Surfaces by Infinite Dilution Chromatography", *Chromatographia*, 3(9-10), 441-444.

Inverse gas chromatography at infinite dilution has been used to study the effects of modifications of cationic (montmorillonite) and anionic (hydrotalcite) clays. By using alkanes and alkenes as probe molecules both the dispersive component of the surface energy and the surface acidic sites were characterized. The introduction of polymers into the structure of these minerals significantly changed their chemical character. Carbonization of samples whose interlayer spaces were saturated with polymers

produced new carbon-modified materials. These composite materials became microporous while retaining their initial acid/base surface properties.

Bandosz, T.J., Putyera, K., Jagiello, J., and Schwarz, J.A. (1993), "Application of Inverse Gas Chromatography to the Study of Surface Properties of Modified Layered Minerals", *Microporous Materials*, 1, 73-79.

Activated carbons from different origins have been oxidized with nitric acid at different temperatures. Some of the oxidized samples were heat treated at 873K in inert atmosphere in order to partially reduce their oxidized surface. The changes in the number of surface species were determined by the Boehm titration method and X-ray photoelectron spectroscopy. Gas chromatography at infinite dilution and finite concentration was used to study the effect of surface groups on adsorption properties of the carbon samples. Oxidation was followed by decreases in the enthalpies and free energies of alkane adsorption. The results obtained indicate that surface chemical groups may hinder and/or perturb occupancy of adsorbed molecules on their energetically most favorable positions.

Bandosz, T.J., Jagiello, J., and Schwarz, J.A. (1993), "Effect of Surface Chemical Groups on Energetic Heterogeneity of Activated Carbons", *Langmuir*, 9, 2518-2522.

The relationship between adsorption energy and micropore sizes is based on the dependence of the molecule-pore interaction potential well depth as a function of the pore width. The adsorption integral equation is used to analyze experimental adsorption isotherms of several simple gases measured at supercritical and near-critical temperatures on two microporous carbons. It is observed that the adsorption systems are strongly heterogeneous from the standpoint of their adsorption energetics which are characterized by asymmetrical energy distributions with a broadening toward high energies. It is also shown that these distributions correspond to relatively narrow and symmetrical peaks characterizing the distribution of pore sizes. The strong asymmetrical

relationship between adsorption energy and pore width magnifies the energetic heterogeneity even though pore size distributions show only modest dispersion.

Jagiello, J., and Schwarz, J.A. (1993), "Relationship Between Energetic and Structural Heterogeneity of Microporous Carbons Determined on the Basis of Adsorption Potentials in Model Micropores", *Langmuir*, 9, 2513-2517.

In order to use hydrogen as an energy carrier in modern energy-use systems, it is necessary to find compact, efficient means for storing hydrogen for mobile and/or stationary applications. Performance evaluations, coupled with cost analyses for four major alternatives for hydrogen storage show that activated carbon based storage compares quite favorably with the other three options: pressurized cylinder, metal hydride, and liquefaction. Gravimetric, volumetric, and modified volumetric laboratory experiments are able to assess the storage properties of various activated carbons and ultimately identify which carbons and which pressure and temperature windows meet desired storage requirements.

Schwarz, J.A., and Amankwah, K.A.G. (1993), "Hydrogen Storage Systems", *Future of Energy Gases*, in press.

The sorption properties of carbon-composite materials based on montmorillonite and hydrotalcite matrices have been studied using nitrogen adsorption isotherms and inverse gas chromatography. Carbon composite materials derived from both types of inorganic precursors contain pore structure accessible for adsorbate molecules. Adsorption capacity per unit mass of these composite adsorbents is larger in the case of hydrotalcite than montmorillonite based materials. Exposing these materials to ambient conditions results in their hydration. Subsequent water removal by heating under vacuum increases nitrogen adsorption capacity which is explained by the opening of the adsorption space. The water content of hydrated samples and its effect on adsorption capacity is greater

for the case of hydrotalcite based materials. No direct relationship between carbon content and adsorption properties of the materials studied is observed.

Putyera, K., Bandosz, T.J., Jagiello, J., and Schwarz, J.A. (1993), "Sorption Properties of Carbon Composite Materials Formed from Layered Minerals", *Clay and Clay Minerals*, in press.

A method for characterization of carbon surfaces' acidity using a continuous distribution of acidity constants is proposed. The method is based on potentiometric titration measurements. Titration curves are transformed into proton adsorption isotherms, and are analyzed to yield the distribution of acidity constants. Calculation of the distribution function is sensitive to experimental errors, and therefore a careful smoothing treatment must be applied to the experimental data. The method is tested by application to organic compounds, and the calculated pK values are in excellent agreement with literature data. The method is then applied to study the evolution of acidic groups, in terms of their pK values, subsequent to modification processes such as oxidation and reduction of activated carbons. It is demonstrated that the method is sensitive to the changes in the number and character of surface acidic groups.

Bandosz, T.J., Jagiello, J., Contescu, Cr., and Schwarz, J.A. (1993), "Characterization of the Surfaces of Activated Carbons in Terms of Their Acidity Constant Distributions", *Carbon*, 31(7), 1193-1202.

A sodium form of Wyoming smectite was intercalated with hydroxyaluminum cations and saturated with furfuryl alcohol; polymerization and carbonization were done to obtain carbon-smectite composites. Carbons were obtained from the smectite inorganic matrices by washing them with HCl and HF. The synthesized materials were studied by X-ray diffraction, inverse gas chromatography, DTA, and adsorption of nitrogen and

methane. Analysis of data indicates the presence of small micropores inside the carbon-smectite composites and in the carbons washed from their inorganic matrices.

Bandosz, T.J., Putyera, K., Jagiello, J., and Schwarz, J.A., "A Study of Carbon-Smectite Composites and Carbons Obtained by In-Situ Carbonization of Polyfurfuryl Alcohol", Carbon, in press.