THE microReport

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The Science and Technology of Small Particles™

MICROMERITICS INSTRUMENT CORPORATION

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In This Issue

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Micromeritics to Showcase New Instruments at the 2006 Pittsburgh Conference

Visit us at PITTCON® 2006 and explore the latest developments in laboratory science.

Pittcon (March 13 - 16 in Orlando, Florida) is one of the world's premier annual conferences devoted to laboratory science and instrumentation. It's a great opportunity to get a hands-on look at "the latest and greatest," and to interact face-to-face with our technical, sales, and customer support associates.

Micromeritics, located in booths 3632 and 3633 at the Orange County Convention Center, will showcase several new instruments at this year's exhibition, including the Elzone® II 5390 Particle Size Analyzer, the ElectroPrep, the Gemini VI, and the recently released ASAP 2420.

The Elzone II 5390 Particle Size Analyzer, utilizes the electrical sensing zone method to size samples without being affected by optical properties, densities, colors, and shapes. The Elzone quickly and accurately determines the size, number, concentration, and mass of a wide variety of organic and inorganic materials. Easy-to-use automated features include: start-up, run, and shut-down routines; blockage detection and clearing; flushing/rinsing; and calibration. The Elzone determines particle size in a range suitable for a wide variety of industrial, biological, and geological specimens. A high level of accuracy, resolution, speed, ease-of-use, and a compact size make the Elzone equally suitable for industry, quality control, and research and development laboratories.

Elzone II 5390

continued on page 2

Pittcon continued

The Gemini VI Surface Area Analyzer boasts improvements that benefit those applications requiring extended analysis time and high stability. Upgrades from the Gemini V include a larger cabinet which allows for longer sample tubes and a larger, taller Dewar. The new larger Dewar not only extends the life of the cryogen bath, but also provides a very stable thermal environment in which to measure the isotherm. The results are improved repeatability from one sample to the next and sufficient analysis time for a complete adsorption - desorption isotherm. Another improvement is the capability to monitor continuously the saturation vapor pressure (P_0) of the adsorptive using a dedicated P_0 tube and transducer. The result is a more meticulously determined relative pressure.

These improvements combined with features such as automatically generated or user-defined pressure tables with user-selected endpoints, free-space determination and correction options, and a variety of reports make the Gemini VI a valuable tool for the determination of surface area and pore size distribution.

The ASAP 2420 Accelerated Surface Area and Porosimetry System introduced in January will be featured at Pittcon as well. This powerful instrument is specifically designed for laboratories where high sample throughput is a strategic priority.

With six independently operated preparation and analysis ports, a new analysis can begin as soon as another is finished. This provides an important advantage over many multiport instruments that require all samples to be prepared or analyzed at the same time.

Another key, standard feature of the ASAP 2420 is a programmable and fully automated sample preparation module with twelve independently operated ports. Samples may be added or removed from degas ports without disturbing the treatment of other samples undergoing preparation or analysis.

Accurate extended analysis is accomplished with larger Dewars and Isothermal jackets.

In addition to typical reports such as BET and Langmuir surface area, t-Plot, and BJH pore size distribution, the ASAP 2420 also features the STSA thickness curve, and DFT pore size and surface energy reports.

High throughput, reliability, versatility, and high quality data describe the new ASAP 2420.

The new **ElectroPrep ™** provides a constant supply of filtered electrolyte for the Elzone II 5390. The ElectroPrep recirculates electrolyte through a filter cartridge that retains particles greater than 0.1 to 0.2 micrometers in diameter. In typical usage, one preparation of electrolyte may last for several months.

Visit us at booths 3632 and 3633 for more information about these and other products, or visit www.micromeritics.com.

Diffusion of Nitrogen and Methane in Clinoptilolites - Tailored for N_2/CH_4 Separation

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Introduction

Upgrading production from the aging natural gas wells by non-cryogenic separation of nitrogen from methane continues to be a topic of intense research. New nano-structured sorbent materials have been developed in the recent past for the purpose of separation of nitrogen/methane mixtures by pressure swing adsorption (PSA). Ackley and Yang have demonstrated the use of carbon molecular sieve (CMS) for this purpose but have also shown that the potential for CMS to achieve the pipeline quality is doubtful [1]. Habgood developed a process using 4A molecular sieves for the same separation, but this process was limited to low temperatures (273 K) and high methane content [2]. Although separation can often be improved through process optimization, maximum performance is limited by the adsorption characteristics of the sorbent. More promising separation of N_2/CH_4 mixtures was achieved by PSA using calcium-exchanged clinoptilolite, which is a naturally occurring zeolite [3]. The Molecular Gate Technology is the most promising process available commercially at present for N_2/CH_4 separation and it uses Sr-ETS-4 calcined at 315 °C [4].

Clinoptilolites have a two-dimensional channel structure with multiple indigenous cations located in these channels that can be systematically altered to get desired adsorption characteristics by performing ion exchange [5]. One of the objectives of this work is to prepare mixed ion-exchanged clinoptilolites (i.e., partially exchanged clinoptilolites) and test their effectiveness for CH_4 enrichment by means of adsorption measurements. In this study various ion-exchanged forms of clinoptilolites are prepared and the low-pressure adsorption kinetics of nitrogen and methane in them is studied using Micromeritics' ASAP 2010 (constant volume apparatus).

Experimental

Clinoptilolite (TSM 140 D clinoptilolite) supplied by Steelhead Specialty Minerals (Spokane, WA) was used. The raw clinoptilolite was crushed to 140 mesh, purified and then subjected to ion exchange with various salt solutions following procedures described elsewhere [6]. Partially exchanged and mixed ion exchange clinoptilolites were prepared by sequential ion exchange, complete details given elsewhere [6,7].

Natural Gas Well

The rate of adsorption of nitrogen and methane on the various clinoptilolite samples prepared were measured using Micromeritics' ASAP 2010 system, equipped with the Rate of Adsorption (ROA) software. Prior to measurements, the clinoptilolites were dehydrated in vacuum at 350 °C. All diffusion data were measured at a stepped pressure increment, from 0 to 0.05 atm. For each pressure increment the ROA software reports the amount adsorbed as a function of time. From this the fractional uptake is calculated as follows:

$$f = \frac{m_t}{m_{t\to\infty}} = \frac{\text{qty ads. @ t}}{\text{qty ads. @ equil.}}$$

Whereas, fractional uptake (f) equals the quantity adsorbed at time divided by the quantity adsorbed at equilibrium.

Figure 1

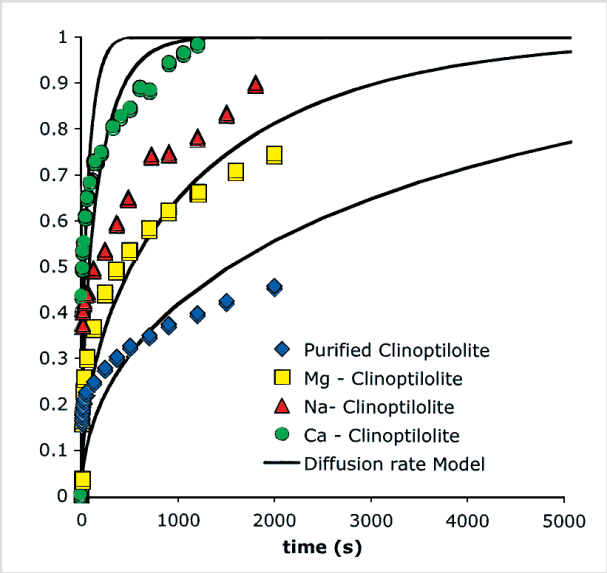

Figure 2

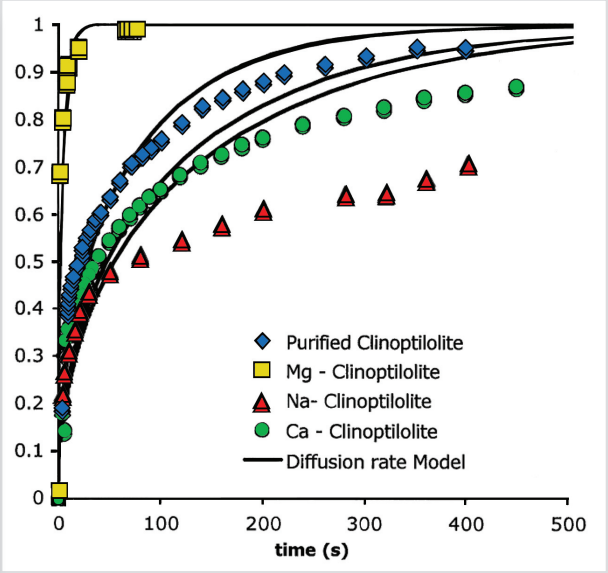

Figure 1 Nitrogen and Figure 2 Methane; both showing uptake on purified clinoptilolite, magnesium clinoptilolite (Mg – Clinoptilolite), sodium clinoptilolite (Na – Clinoptilolite) and calcium clinoptilolite (Ca – Clinoptilolite) along with their fitted diffusion rate model.

The initial few data points were not used in the analysis since there are interfering dynamics in them; namely, *system dynamics* – due to the rapid expansion of the gases when dosing the sample chamber; and *sensor dynamics* – due to the transducer diaphragm being subjected to rapid pressure change. Calibration of these interferences was carried out by doing blank adsorption runs on the Micromeritics ASAP 2010 with aluminum foil and the dynamics were found to last for a maximum of 4 seconds. Hence the Micromeritics ASAP 2010 could be used with confidence for ROA measurements where the time scale of adsorption differs from that of the interfering dynamics by orders of magnitude. Diffusion time constants were then calculated by fitting experimental fractional uptake data with the solution of the diffusion equation for spherical particles [8].

Results and Discussion

Figures 1 and 2 show nitrogen and methane uptake curves on some of the clinoptilolite samples, respectively. The diffusional time constants for nitrogen and methane uptake along with their kinetic selectivity on various clinoptilolite samples are given in Table 1. We could see that nitrogen diffuses faster than methane in most of the clinoptilolites and the diffusional time constants differ by orders of magnitude depending on the exchange cation. Clinoptilolite framework consists of two parallel channels of ten-member (Channel A) and eight-member (Channel B) rings that are connected to a third eight-member ring (Channel C). The cations compete for cation exchange sites that are located in these three channels. In both Ca-exchanged clinoptilolite and Na-exchanged clinoptilolite, the nitrogen diffusion is slower by a couple of orders of magnitude compared to other clinoptilolites implying severe pore blocking in the channels occupied by the Ca2+ and Na+ cations (Channels A and B). The fit of the rate model for nitrogen uptake is poor in Na – Clinoptilolite due to the severe pore blocking in channels A and B (explained earlier) while channel C is open which gives rise to rapid initial uptake of both nitrogen and methane. In K – exchanged clinoptilolite samples, both nitrogen and methane diffuse faster since K+ cations occupy

Sorbent	D/R2 (1/s)		Kinetic selectivity
	Nitrogen	Methane	
Purified Clinoptilolite	1.1 x 10-3	2.0 x 10-5	55
Mg – Clinoptilolite	1.8 x 10-2	6.0 x 10-5	300
K – Clinoptilolite	2.2 x 10-2	5.8 x 10-4	37.9
Li – Clinoptilolite	6.2 x 10-3	3.8 x 10-4	16.3
Na – Clinoptilolite	5.6 x 10-4	4.1 x 10-4	1.4
Ca – Clinoptilolite	6.5 x 10-4	1.1 x 10-3	0.6
H – Clinoptilolite	2.8 x 10-2	3.2 x 10-2	0.9
Mg/Ca (20/80) Clinoptilolite	4.0 x 10-3	6.5 x 10-4	6.2
Mg/Ca (50/50) Clinoptilolite	1.5 x 10-3	6.5 x 10-3	0.2
Mg/Ca (80/20) Clinoptilolite	1.7 x 10-3	6.9 x 10-3	0.2
K/Na (20/80) Clinoptilolite	1.2 x 10-2	1.4 x 10-4	85.7
K/Na (50/50) Clinoptilolite	3.4 x 10-2	2.4 x 10-4	141.7
K/Na (80/20) Clinoptilolite	4.5 x 10-2	3.2 x 10-4	140.6
Mg/Na (210/80) Clinoptilolite	6.0 x 10-3	4.5 x 10-5	133.3
Mg/Na (50/50) Clinoptilolite	6.5 x 10-3	9.0 x 10-5	72.2
Mg/Na (80/20) Clinoptilolite	6.8 x 10-3	2.8 x 10-5	242.9
Na/Li (20/80) Clinoptilolite	5.0 x 10-3	1.8 x 10-5	277.8
Na/Li (50/50) Clinoptilolite	1.7 x 10-3	6.0 x 10-5	28.3
Na/Li (80/20) Clinoptilolite	1.4 x 10-3	2.1 x 10-4	6.7
Ce – Clinoptilolite #1	8.0 x 10-3	9.8 x 10-5	81.6
Ce – Clinoptilolite #2	8.0 x 10-3	9.8 x 10-5	81.6
Ce – Clinoptilolite #3	8.0 x 10-3	2.4 x 10-4	33.3
Sr – Clinoptilolite	9.5 x 10-3	1.2 x 10-5	791.7
Ba – Clinoptilolite	1.4 x 10-2	1.2 x 10-3	11.7

Table 1. Diffusion time constants and kinetic selectivity for nitrogen and methane uptake in various clinoptilolites.

site M(3) that, in turn, open up the ten-member ring (Channel A). Mg – exchanged clinoptilolite shows the maximum kinetic selectivity among the clinoptilolite samples studied here, since Mg2+ cations occupy site M(4) located in Channel A, which would ensure molecular sieving of methane in the ten-member ring channel. The adsorption measurements in Micromeritics' ASAP 2010 aid in understanding the cations, their exchange sites, and their influence on adsorption and diffusion characteristics in clinoptilolite samples, which can be used to tailor the clinoptilolite samples for specific separation needs.

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Micromeritics Analytical Services incorporates additional state-of-the-art equipment to better serve our customers. These improvements are designed to increase the quality of results, enhance customer service, and decrease sample turnaround-times. Several new analyses have been added to better serve your needs. These new analyses are highlighted in the new price list and in the online product catalog. You can obtain a copy of the new price list by contacting our laboratory.

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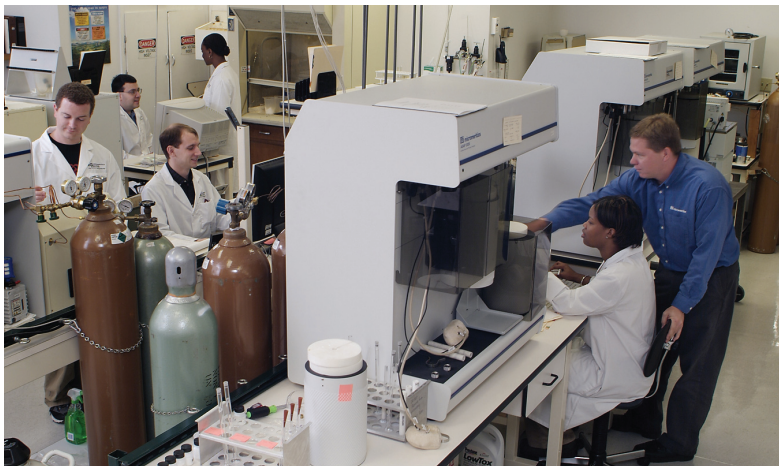

Our analysts use a Micromeritics ASAP 2020 to measure a hydrogen adsorption isotherm. Recent upgrades allow for proper dosing and reporting of the hydrogen quantities adsorbed. Typical reports include the weight percent of hydrogen adsorbed and the Pressure Composition Isotherm that is frequently used by hydrogen storage researchers.

The Micromeritics Analytical Services web site has been modified to reflect new specification sheets highlighting some of these new analyses. Look for these helpful documents on our home page in the quick download section, *www.particletesting.com*.

Hydrogen capacity and composition isotherms for fuel cell research, and "All Shapes and Sizes" which discusses different techniques for measuring particle size

Mark your calendars.

Micromeritics Analytical Services will be exhibiting at the 2006 Spring National Meeting of the American Chemical Society. The exhibition and meeting will be held in Atlanta, GA March 26 – 30. Stop by our booth, Booth 331, and see what is new.

Finally, Micromeritics Analytical Services would like to thank all our customers who have trusted us with their valuable samples in 2005. We appreciate your business and look forward to working with you again

Greg Thiele
Business Manager

Micromeritics Instrument Training Courses

Training is provided for most Micromeritics instrumentation at the time of installation. This training presents all the information required for a new operator to quickly become proficient operating the instrument. In cases where personnel changes occur or more advanced training is required, Micromeritics conducts a variety of classes for many of our instruments. These courses are held at our headquarters in suburban Atlanta, Georgia. The courses include:

Detailed Operational Procedures
Items covered are effective sample file creation, use of analysis parameters, and manual sample entry. You´ll learn how to utilize the full power and flexibility of the operating software.

Automatic Analysis
Develop correct analysis procedures to optimize collection of accurate, reproducible data. Much of the class time is spent performing analyses in a controlled, tutorial environment.

Systems Utilities
Discover all of the instrument software utilities which help you manage sample information files and directories, protect data, and select system options.

Troubleshooting
Learn techniques that enable you to locate and quickly resolve instrument problems.

Report Generation and Comprehension
Learn to configure reports and obtain more useful information, as well as improve comprehension of the reports produced.

User Maintenance
Practice routine maintenance procedures which improve operation, reduce downtime, and increase data accuracy.

Theory Overview
Learn about the scientific theory upon which each instrument is based and how it applies to the critical factors relevant to successful sample preparation and analysis performance.

Enrollment
Training courses last from 2 to 3 days and are designed to provide hands-on, performance-based instrument knowledge. Small classes guarantee close individual attention. Included in the course materials are a Study Guide, an instrument Operator´s Manual, and other handout materials. Certificates of Completion are also awarded to all trainees.

Training 2006

ASAP 2020 Physi/Chemi Combined
February 28 - March 3

Gemini V
April 11 - 12

TriStar 3000
May 23 - 25

For additional information or to register for the class of your choice, contact the Micromeritics Training Department at 770.662.3607. Early registration is recommended since class space is limited.

See our web-site for complete course schedule.
www.micromeritics.com

Below are students attending the recent AutoPore IV course. Left to Right: Noel Baker, Bill Kopeski, Oliver Urbanek and Lauren Reimer.

Events

Pittcon 2006
March 13 - 16, 2006
Orange County Convention Center
Orlando, FL

Interphex 2006
March 21 - 23, 2006
Jacob K. Javits Convention Center
New York, NY

American Chemical Society Meeting and Exposition
March 26 - 30, 2006
Georgia World Congress Center
Atlanta, GA

Technoceramica
April 4 - 7, 2006
Expocentre
Moscow, Russia

Nanotech 2006
May 7 - 11, 2006
John B. Haynes Veteran's Memorial Convention Center
Boston, MA

International Powder & Bulk Solids Exhibition 2006
May 9 - 11, 2006
Donald E. Stephens Convention Center
Rosemont, IL

See our web-site for a complete Event schedule www.micromeritics.com

Attention Authors

We welcome articles and information concerning particle technology applications performed with Micromeritics instrumentation. Everything from a single plot with operating conditions to an in-depth article on physisorption, chemisorption, etc. with supporting plots will be considered. If your material is published in The microReport, you will receive a copy of Analytical Methods in Fine Particle Technology by Paul A. Webb and Clyde Orr.

Send your article to:
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Include your title, return address and phone number. Contributions cannot be returned, but each will be acknowledged.

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