Characterization of Mixed Micro- Meso-porous Catalysts for Membrane Applications

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Introduction

New porous catalyst and separation materials such as SBA-15, PHTS and FDU type silicas have recently been developed. These materials possess a complex porous structure of both micro- and meso-pores. The mesopores provide facile access to the micropores wherein shape selective catalysis might occur. These materials require new careful analytical techniques to separate the microporous and mesoporous components of the structure, in order to give valid estimations of the surface areas and pore distributions. As an example, the surface areas calculated by BET analyses for these materials are grossly incorrect as they are for the analysis of zeolite isotherms. We have developed a combination of three techniques to achieve this purpose. Namely, employing pre-adsorption to separate the mesoporous nature of the materials from the micropore component (<2 nm). Secondly the use of an accurate empirical model to estimate the micropore size distribution of a non-crystalline microporous solids, such as SBA-15.(*1, 2*) Thirdly, incorporating a novel technique which has been developed to measure porous structure of intact membranes and supported catalyst materials. The technique involves a specially designed re-sealable cell in which the membrane can be placed followed by the measurement of high resolution adsorption. This technique has been successfully demonstrated on alumina supported silicalite membranes of differing geometries.(*3, 4*)

Materials and Methods

SBA-15 materials were prepared based on the work by Luan et al.(*5*) employing both conventional and microwave heating. Plugged hexagonal templated silicas (PHTS),were prepared in accordance with the procedure described by van der Voort et al.(*6*)

Adsorption and desorption isotherms were measured at the boiling point of nitrogen (77 K) and argon (87 K) using an AUTOSORB-1-MPC (Quantachrome Instruments; Boynton Beach, FL) gas adsorption system or our own high-resolution adsorption equipment as described in Refs. (*7*) and (*8*). Nitrogen and argon were used as adsorbates, and a constant level of the liquid N_2 or Ar bath was maintained during all measurements. Dead space measurements were conducted using helium; saturation pressures were determined by condensing/subliming the adsorbate in a separate vessel inside the cryogenic bath at intervals throughout the experiment or by condensing/subliming adsorbate in the sample container at the end of the experiment. All gases used in the experiments are ultra-high purity.

Pre-adsorption was performed procedure provided by Sayari et al(*9*). for the sequential adsorption experiments with little alteration. Argon or nitrogen adsorption isotherms were obtained from the AUTOSORB®-1-MPC instrument and n-nonane vapor adsorption was performed using the VAS(*8*). Samples of 30~90 mg was placed in a glass adsorption sample cell (1/4_ outside diameter stem) with stopcock (1/4_ outside diameter stem), where sample cell and stopcock were connected by Ultra-Torr® union (1/4_ tube outside diameter) with appropriate size Viton® o-rings. All the samples were outgassed at 300°C for 12~20 hours prior to the adsorption experiments. N-nonane (99%) was obtained from Acros and used as received.

Results and Discussion

Complex micro-meso-materials included SBA-15 and PHTS were investigated using a combination of techniques. Figure 1 shows the argon adsorption isotherms of an SBA-15 material, before and after preadsorption of nonane. The micropours component can be masked (filled) leaving the mesoporous structural component the same under analysis by argon adsorption. The mesopore distribution can then be determined using standard BJH analysis. Micropore distributions were then determined using a empirical model developed at UMass.(*1*)

These new catalysts materials in the form of supported membranes are investigated using the intact cell setup described above.

Significance

Many new microporous catalyst materials such as SBA-15 type meso-microporous systems are being developed and employed in the catalytic and separation industry. The accurate estimation of the pore size distributions of these complex materials is critical in order to fully utilize the structural properties of these systems. These techniques enable a quick and accurate determination of micropores and mesopores in a network from isotherms.

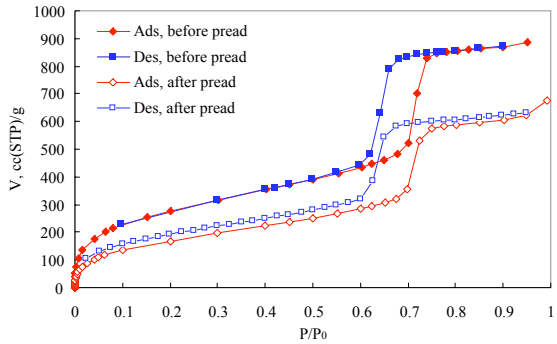

Figure 1. Argon adsorption at 87 K on SBA-15 sample before and after n-nonane pre-adsorption as volume adsorbed versus relative pressure.

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