

Title: Ceramic Membranes for Hydrogen Production from Coal

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Abstract

Dense, supported silica membranes have been previously reported having high selectivity for hydrogen separation from coal gas or synthesis gas at high temperatures. The supports used in most of these previous studies were Vycor glass tubes of about 1 mm wall thickness and uniform pore size 4-5 nm. The low permeance of these support tubes (about 3.5 MPU) limited the permeance of the final membrane to below 3.5 MPU no matter how thin the permselective layer was ($1 \text{ MPU} = 10^{-8} \text{ mol/m}^2\text{-s-Pa}$). To increase the membrane permeance to commercially useful levels it is necessary to use asymmetric supports that have micrometer-sized pores everywhere except in a thin skin of nanometer-sized pores. In this project it was originally planned to develop such highly permeable supports by coating macroporous alumina tubes with a thin layer of Vycor glass having 1-3 nm pore size. The same support function could be served by a thin zeolite layer coated onto macroporous alumina. As the zeolite coating turned out to be simpler to make than the Vycor glass coating, we have chosen to develop zeolite-coated alumina as the membrane supports. In the final step, an ultrathin layer of dense, hydrogen permselective silica will be applied on the zeolite substrate using chemical vapor deposition.

So far in this project we have developed zeolite ZSM-5 coatings on porous alumina tubes (1 μm pore size). At ambient temperatures the hydrogen permeance of the

bare alumina tubes is over 1000 MPU, and the hydrogen permeance of the composite zeolite-alumina tubes is about 50 MPU. The zeolite layer is not by itself permselective because in addition to the zeolitic pores of about 0.55 nm it has nonzeolitic pores of about 1-2 nm. But its small pore size and its thermal stability make it suitable as a support for chemical vapor deposition of dense silica.

The key advance made in the development of the composite supports was to deposit the zeolite layer inside the pores of the alumina rather than as an external layer. The internal location of the zeolite layer makes the support more permeable and more resistant to crack formation during calcination or other thermal cycling. Briefly, the composite supports were made using the following procedure. A colloidal suspension of zeolite crystallites about 0.1 μm size was first prepared by hydrothermal growth and used to seed the pore surface of the alumina. Seeding was carried out by simple immersion in the suspension relying on capillary flow to carry the seeds to the internal pore surface. The crystallites were subsequently grown hydrothermally to narrow the support pore size down to 1-2 nm over a thickness of about 10 μm . After growth the supports were dried and calcined to remove the organic template employed in the growth solution. The composite support tubes were characterized by gas adsorption and gas permeation.