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CERAMIC MEMBRANE ELABORATION USING SUPERCRITICAL FLUID

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ABSTRACT

Macroporous alumina supports were prepared from commercial δ-Al_2O_3 and modified by hydrolytic decomposition of titanium isopropoxide in supercritical propan-2-ol. Various experimental parameters were studied in relation to the deposition of TiO_2 particles on the substrate surface and inside the pores: temperature, precursor concentration, water-to-alkoxide ratio, solution flow rate, and deposition time. A set of these parameters was found to allow supported membranes with high nitrogen permeation (9.5×10^{-6} mol·m^{-2}·s^{-1}·Pa^{-1}) and low average pore radius (1.5 nm) to be obtained. *© 2000 Elsevier Science Ltd*

KEYWORDS: A. ceramics, A. thin films, B. sol-gel chemistry, C. electron microscopy

INTRODUCTION

The application of porous inorganic membranes in filtration and catalytic reactions has attracted much attention because of their high thermal, chemical, and mechanical stability. Supported membranes exhibit very low pore size (in the nanometer range) and high selectivity while keeping high permeability. They are obtained from a macroporous ceramic support treated in such a way that nanoparticles can be deposited either as a thin film on the surface or inside the pores in order to decrease their diameter. In the first case, sol-gel

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techniques, either colloidal or polymeric, have been used widely [1–7]. In such processes, a sol must first be prepared under controlled conditions. After coating, drying has to be performed very slowly at room temperature before calcination, usually above 400°C, in order to obtain crystallized oxide.

Numerous studies have been conducted by various laboratories to get a better understanding of the chemical and physical phenomena involved during the sol transformation and to develop specific strategies leading to controlled pore sizes for flaw-free supported ceramic membranes [2]. First, a variety of deposition techniques, in addition to the initial slip casting method, such as deep coating, filtration deposition, and permformation, has been proposed [6]. Second, many metal oxides used as membrane materials (alumina, titania, zirconia) exhibit a structural phase transformation between 450 and 900°C, which favors crystallite growth and sintering [5]. In order to obtain crack-free membranes and to improve their thermal stability, many precautions must be taken during the drying and calcination steps. Phase transformation must be retarded at higher temperature, for example, by using a doping oxide [5] or avoided by starting with a suitable sol (rutile sol in the case of TiO_2 membrane) [7]. Such a route to modify supports to obtain membranes for ultra- or nano-filtration is very time-consuming, but a pore diameter in the deposit can be lowered to 3–5 nm. However, to prevent crack formation, the optimum thickness of the layer obtained under each coating treatment is claimed to be less than 0.2 μm [4].

Another route to reduce pore size is the chemical vapor deposition (CVD) process. Reaction between two reactive gas flows usually leads to the formation of already crystallized metal oxide particles. In the "classical" method, streams are supplied on the same side of the support: reaction occurs at the corresponding surfaces and substrate pores are covered or plugged. In a "modified" CVD method, reactant flows counterdiffuse from both sides of the membrane and react when they contact each other on the inner surface of the pores. Comparing the two methods with the $SiCl_4/H_2O$ system, it has been shown that a one-sided membrane has significantly higher selectivity for H_2/N_2 separation [8]. However, it has been noted that, in the counterdiffusion technique, silica formation in zeolite materials can be controlled by the molecule size of the reactant [9]. This last process has been used for TiO_2 and ZrO_2 deposition either inside the pores of the substrate (pore diameter $>$ 100 nm) or in the supported top layers of the membrane with smaller pore size ($<$20 nm) and thickness (about 5 μm) [10,11]. Reaction between the two gas flows (metal chloride in argon and water in air) was conducted between 700 and 1000°C during a relatively short time (about 20 min). Metal oxide deposition was found at the substrate surface exposed to the metal chloride vapor, and a kinetic study showed that it proceeded according to a heterogeneous reaction [10]. Pore reduction observed from gas permeation measurements was shown to strongly depend on the initial pore size distribution, but no final diameter values were reported [11].

Recently, a new method to modify the pore size distribution of ceramic membranes, using a supercritical fluid solution of a metal oxide precursor (such as metal alkoxide) infiltrated through the macropores was proposed [12]. The infiltrated samples are further immersed in water vapor for complete hydrolysis and finally dried and treated at 450°C in order to obtain the final products. Propane used as solvent is saturated with aluminum isopropoxide at 130°C under 30 MPa and infiltrated into α-Al_2O_3 membranes under the same pressure and temperature conditions. During the infiltration, the pressure of the supercritical solution falls off along the flow direction, and solute supersaturation is reached inside the pores. It has been shown that either homogeneous or heterogeneous nucleation can then occur. The first mechanism is observed when the surface energy of alumina support is lowered before