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## CATALYZED CO<sub>2</sub>-TRANSPORT MEMBRANE ON HIGH SURFACE AREA INORGANIC SUPPORT

### CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of, and claims priority to, U.S. patent application Ser. No. 12/470,294, filed on May 21, 2009, and claims the benefit of U.S. Provisional Patent Application No. 61/259,861, filed Nov. 10, 2009, which are both hereby incorporated by reference in their entireties.

### ACKNOWLEDGMENT OF GOVERNMENT SUPPORT

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### TECHNICAL FIELD

This application discloses immobilized liquid fluid membranes and methods of making the same, and particularly discloses immobilized liquid fluid membranes including modified, porous metallic substrates for carbon dioxide separation.

### BACKGROUND

Membrane separation is intrinsically energy efficient. Almost all separation processes in living biological systems are performed through a membrane. At present, there exist grand challenges in both membrane materials and design for effective gas separation, particularly for CO<sub>2</sub> separation and more particularly for CO<sub>2</sub> separation from flue gas stream mixtures. Due to the low partial pressure of CO<sub>2</sub> in flue gas mixtures, and the huge gas volumes, a great quantity of membrane surface area is typically needed for the separation process. While certain CO<sub>2</sub>/N<sub>2</sub> selectivity is necessary, high permeance is an important factor for reduction of membrane surface area, module volume, and cost for making such separation devices on a commercial scale.

Polymeric membranes based on glassy polymers such as cellulose acetate, polyimide, and poly(phenylene oxide) (PPO) are commercially available products for separation of CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> pairs. However, such polymers show decreased performance in presence of water vapor due to competitive sorption between water and permeate gases. These commercially available membranes also have low CO<sub>2</sub> permeance under flue gas conditions.

Poly(vinyl alcohol) (PVA) membranes and other polymeric membranes have been tried. However, PVA-based membranes require separation temperatures above 100° C., which is well above flue gas temperatures. Certain thin PVAm/PPO composite membranes (molecular polyvinylamine coated with poly(phenylene oxide)) have been alleged to operate at 25 to 40° C.—within the flue gas temperature range. However, these membranes require a presence of a large fraction of moisture in the feed gas and/or sweep gas to keep the separation membrane layer wetted or swollen. As water permeance is much higher than CO<sub>2</sub>, a large volume of water must be introduced into the feed gas to keep the membrane fully wetted. For a given PVAm/PPO membrane, the

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CO<sub>2</sub> permeance decreases by nearly three orders of magnitude as the feed gas relative humidity (RH) was reduced from 90% to about 25%.

A few inorganic membranes have been investigated for use as CO<sub>2</sub> separators. It has been reported that molecules can be separated over a silicalite membrane based on differences in molecular weight as well as size or shape. The ZSM-5 (zeolite sieve of molecular porosity—5) type zeolite membranes shows only moderate CO<sub>2</sub>/N<sub>2</sub> or CO<sub>2</sub>/He selectivity at low CO<sub>2</sub> feed pressures, which falls short of the flue gas separation needed (CO<sub>2</sub>/N<sub>2</sub> selectivity greater than 50).

What is needed are membranes and methods for making the same, which membranes provide improved stability, high CO<sub>2</sub> permeation flux, and cost-effective manufacturability for commercial-scale use for separating CO<sub>2</sub> from gas streams such as flue gases.

### SUMMARY

Presently disclosed are carbon dioxide separation membranes, membrane modules for industrial-scale use, and methods of making the same, which new membranes provide superior stability, CO<sub>2</sub> permeation and are cost-effective to make and use on a commercial scale for effectively separating CO<sub>2</sub> from gas streams such as flue gas streams. High CO<sub>2</sub> permeation flux is achieved by immobilizing an ultra-thin, preferably catalyzed fluid layer (typically less than 60 μm thick) onto a macro-porous inorganic substrate, which in turn has been modified with a micro-porous or meso-porous modification layer, such as a metal oxide or a ceramic modification layer. The CO<sub>2</sub>-selective liquid fluid is immobilized within the pores of the modification layer or within the pores of the support to block any gas transport pathways that are not selective toward CO<sub>2</sub> permeation over the other molecules, such as gas-phase diffusion and viscous flow. The membrane structure immobilized by a liquid fluid leaves the transport through the liquid fluid as the dominating mechanism for CO<sub>2</sub> molecules to move from the feed side of the membrane to the permeate side of the membrane under a driving force of chemical potential gradient such as partial pressure differential of CO<sub>2</sub>. The immobilized liquid fluid selectively absorbs CO<sub>2</sub> from feed gas mixtures such as flue gas mixtures, allows fast diffusion of the dissolved (or reacted) CO<sub>2</sub> species across the thickness of the liquid fluid, and desorbs CO<sub>2</sub> in the permeate side.

Embodiments of the disclosed membranes have CO<sub>2</sub> permeance levels of 1.0×10<sup>-7</sup> mol/(m<sup>2</sup>sPa) or better. The present membranes provide a cost savings for manufacturing for commercial scale use of up to or exceeding 60% as compared to the conventional separation devices.

Embodiments of the disclosed membranes may comprise a porous, thin-metallic substrate or support sheet, a porous metal oxide or ceramic modification layer on the metal substrate and a CO<sub>2</sub>-selective liquid fluid being incorporated into the formed inorganic substrate. The thin-metal substrate supported membranes provide superior mechanical strength, chemical stability, and high surface area packing density to the immobilized liquid membranes. The metal substrate's surface is modified to change the pore size from macro-porous to micro-porous (less than 1 nm) or meso-porous (a few nms) via a modification layer such as a metal oxide or ceramic modification layer formed thereon. The porous metal substrate, modification layer (modifying the pores of the substrate to provide uniform pore structure for the immobilized CO<sub>2</sub>-selective liquid fluid), and the CO<sub>2</sub>-selective liquid all