Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Surface modification of α-alumina support in synthesis of silica membrane for hydrogen purification

A. Jabbari [a], K. Ghasemzadeh [a,b], P. Khajavi [a], F. Assa [a], M.A. Abdi [a], A.A. Babaluo [a,*], A. Basile [c]

[a] Department of Chemical Engineering, Nanostructure Material Research Center, Sahand University of Technology, Tabriz 51335-1996, Iran
[b] Department of Chemical Engineering, Urmia University of Technology, Urmia 57166-93187, Iran
[c] ITM-CNR, c/o University of Calabria, Via Pietro Bucci, Cubo 17/C, 87036 Rende, CS, Italy

ARTICLE INFO

Article history:
Received 9 March 2014
Received in revised form
6 May 2014
Accepted 10 May 2014
Available online 14 June 2014

Keywords:
Hydrogen purification
Amorphous silica membrane
Aluminum hydroxide
γ-Alumina layer
Activated molecular sieving

ABSTRACT

In this work, an experimental study was carried out on the synthesis of silica membrane for hydrogen purification, in which synthesis of γ-alumina intermediate layer using cheaper and safer source was investigated. For this purpose, aluminum hydroxide was selected and the bohmite sols were prepared by acid or base catalyzed hydrolysis of the different salts for comparing with alkoxide source. The SEM micrographs showed no distinct γ-alumina layer on the substrate coated by base catalyzed sol of salt (sample 1), while a homogeneous γ-alumina layer was formed by acid catalyzed sol of salt (sample 2). After γ-alumina layer formation, the gas permeance mechanism was approximately changed. These results were similar to SEM results and N_2 permeance experiments of sample 3 in which substrate was coated with alkoxide sol. However, the γ-alumina layer of sample 2 had no good adhesion to the substrate. Nevertheless, use of aluminum hydroxide can be promised to synthesis of γ-alumina layer; the membrane was synthesized on the modified support with aluminum tri-sec-butylate sol. In particular, in the synthesized silica membrane as the temperature increases, permselectivity of H_2/CO_2 and H_2/N_2 increases from 4.7 and 7.3 at room temperature to 9.4 and 11.6 at 100 °C and to 23.4 and 31.3 at 200 °C, respectively.

Introduction

Hydrogen as a clean energy carrier, allowing for its reaction with oxygen and generating water as an environmentally friendly exhaust emission, has attracted a great deal of attention around the world in recent years. This is mainly due to the utilization in fuel cell systems and environmental pressures including climate change issues. At the moment, conventional fossil fuel sources are the best economically viable option towards a hydrogen economy [1]. In general, for

---

* *Corresponding author*. Tel.: +98 411 345 9081; fax: +98 411 344 4355.
E-mail addresses: a.babaluo@sut.ac.ir, a_babaluo@yahoo.com (A.A. Babaluo).

http://dx.doi.org/10.1016/j.ijhydene.2014.05.056

hydrogen production from fossil fuels using thermochemical processes, the separation and purification stages are critical technologies. Although Hydrogen can be economically produced by steam reforming processes at rather high temperatures to achieve maximum efficiency [2], to obtain high purity hydrogen during mentioned processes, separation of H_2 from other gas streams such as CO_2 and CO is necessary.

Hydrogen can be purified through several techniques, namely pressure swing adsorption (PSA), cryogenic distillation or membrane separation. PSA and cryogenic distillation processes are commercially available separation techniques, however they are energy intensive [3]. Membrane-related processes are economical [4], environmental and not too much bulky. Furthermore, membrane separation processes consume low energy with the possibility of continuous operation [5]. Membrane based processes are considered to be one of the most promising technologies for the production of high purity hydrogen [6]. It can provide an attractive alternative to PSA and cryogenic distillation, depending on the purity and scale of production [7].

The ceramic membranes owing to their good separation performance, their intrinsic thermal stability and high pressure stability have potential for applications in chemical, petrochemical and energy industry, where gas separation can usually increase the process efficiency under harsh conditions [8]. According to the literature, the microporous ceramic membranes have been considered as one of the candidates for separation problems involving small gas molecules. The main classes of microporous membranes include amorphous silica and zeolite membranes that among them the amorphous silica membranes have been extensively investigated for H_2/CO_2 separation [9]. The silica membranes are usually composite ones consisting of several layers of one or more different ceramic materials [10]. They generally have a macroporous support, one or two mesoporous intermediate layers and a microporous (or a dense) top-layer [10]. The surface modification of inorganic supports, in the fabrication of asymmetric microporous ceramic membrane such as silica membranes, plays a critical role in the synthesis of the homogeneous membrane selective layer. This is due to the defects eliminating and preventing of silica sol particles diffusion in pores of support. The γ-alumina sub-layer is extensively used as an intermediate membrane layer for surface modification in the synthesis of microporous membranes. But this method is well-known as expensive procedure due to the high cost of the γ-alumina precursor and higher humid sensitivity that cause problems with reservation. Moreover, the γ-alumina layer can be prepared by hydrolysis and condensation of aluminum alkoxide precursors such as aluminum-tri-sec butoxide (ASTB), aluminum isopropoxide (AIP) and aluminum-tri-sec-butylate (ASB). Therefore, finding a proper precursor for replacing the alkoxides, can affect the extent of the silica and also other ceramic membranes.

In this study, we tried to find a new precursor for synthesizing γ-alumina layers in silica membranes fabrication. For this purpose, synthesis of silica membrane for hydrogen purification at high temperatures was carried out, in which synthesis of γ-alumina layers was investigated via cheaper and much safer precursors. To surface modification of homemade α-alumina support, after primarily experimental analyses, among different possible sources the aluminum tri-sec-butylate and aluminum hydroxide were selected for a comprehensive investigation. Aluminum hydroxide precursor is much cheaper, has no problems in reservation and also synthesis of γ-alumina layer with this precursor is much easier. However, achieving the stable γ-alumina layers is one of the technical targets for surface modification. After selecting the most proper precursor for γ-alumina layers, the silica layer is coated on the synthesized γ-alumina layers. Finally, the performance of silica membrane for hydrogen separation is studied.

Experimental procedure

Materials

In this experimental study, the material sources used as follows: tetraethyl orthosilicate (TEOS, 98%, Acros) as silicon source, nitric acid (HNO_3, 65%, Merck) and sodium hydroxide (NaOH, 99%, Merck) as catalyst for silica sol preparation, ethanol (EtOH, 99.9%, Merck) as solvent, and polyethylene glycol (PEG, Merck, Molecular weight: 35,000) as stabilizer. Also, aluminum-tri-sec-butylate (97%, Merck) and aluminum hydroxide ($Al(OH)_3$, Merck) as source of γ-alumina.

Membrane supports

The homemade supports used for membrane synthesis were α-alumina tubes with thickness of 4 mm, diameter of 12 mm, length of 70 mm, average pore size of ≈0.57 μm and average porosity of 47.2%. Before the γ-alumina synthesis, the supports were cleaned in distilled water by an ultrasonic regenerator for 10 min and then dried at 40 °C for 12 h.

γ-Alumina sub-layer preparation

After primary investigation on γ-alumina sources, γ-alumina intermediate layer was prepared using two different sources of aluminum-tri-sec-butylate and aluminum hydroxide. The prepared samples were summarized in Table 1, which are presented with more details in the following sections.

γ-Alumina sub-layer preparation with aluminum hydroxide precursor

For γ-alumina intermediate layer synthesis, two different methods were performed in which aluminum hydroxide was catalyzed by acidic or basic catalyst.

γ-Alumina sub-layer preparation with aluminum hydroxide precursor catalyzed by base. The γ-alumina intermediate layer

Table 1 – The details of samples prepared as intermediate layers.

Code	Source	Catalyst
Sample 1	Aluminum hydroxide	Base (NaOH) catalyzed
Sample 2	Aluminum hydroxide	Acid (HNO_3) catalyzed
Sample 3	Aluminum-tri-sec-butylate	–