

Fabrication of asymmetric alumina membranes I. Effect of SrO addition on thermal stabilization of transition aluminas

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ABSTRACT

The effect of SrO addition on the thermal stabilization of transition aluminas with the aim of producing membrane layers (supported and unsupported) has been investigated. Al_2O_3-x wt.% SrO composite powders ($x = 1, 3, 5, 8$) were synthesized by co-precipitation of the hydroxides from solutions of AlCl_3 and $\text{Sr}(\text{NO}_3)_2$ salts using NH_4OH as a precipitating agent. Optimum SrO dopant concentration regarding the transition aluminas stabilization effect was determined to be 5 wt.% based on XRD analysis. STA analysis showed a 30 °C shift versus higher temperatures in the transformation of final transitional alumina (θ - Al_2O_3) to stable alpha phase due to addition of 5 wt.% SrO. The mechanism of transition aluminas thermal stabilization as a result of SrO addition is thoroughly discussed. Unsupported alumina membranes were prepared by drying boehmite sols at 600, 800, 1000 and 1100 °C. The effect of calcination temperature on surface area, pore size distribution of unsupported membranes containing 5 wt.% SrO has been investigated. The microstructure of unsupported and supported membranes revealed quite different. Smaller grains in the supported layers were attributed to the interaction between support and membrane.

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1. Introduction

A membrane is considered to be a semi-permeable barrier between different phases that are not in thermodynamic equilibrium with each other [1]. The principal function of a membrane is to influence the movement of different species to a different extent, thus facilitating preferential mass transport of one (or more) particular species [1]. Many important applications of membranes are energy- or environment-related and in industrial processes they are often employed in addition to conventional separation processes [1]. Membranes can be classified in many different ways, for instance based on their separation characteristics, their structure or the materials they consist of. An important distinction is that between organic and inorganic membranes, organic membranes have a lot of advantages compared to inorganic membranes, of which their low price is certainly an important one [2]. However, organic membranes cannot be used in high temperature applications or in chemically aggressive environments. In those cases one has to resort to inorganic materials. The unique thermal, mechanical and chemical properties of inorganic membranes over polymeric membranes make them good candidates for industrial and harsh environment applications.

Ceramic membrane filters, which are superior in resistance against heat, corrosion and solvent chemical attack, are widely used for filtering. Since the structure of the membrane is hardly changed by pressure and heat, it can be used for a long time [1,3]. From the material point of view, ceramic membranes can be made from different sources. Among them, alumina-based membranes have been already commercialized. As a corollary, in fabricating ceramic bodies, scientists do not like to lose this pioneer material. Alpha-alumina and its related transition phases have widely been used in separation technologies that need nano-scale porosity, high specific surface area and catalytically active surface sites [4]. However, transition aluminas are meta-stable phases, and at about 1000 °C, there is a transformation to α - Al_2O_3 accompanied with a detrimental and drastic loss of specific surface area and change in surface chemistry. Thus, thermal stabilization of transition aluminas so that processes can be shifted to higher temperatures has been of greater interest [4]. Numerous efforts have been made to improve the thermal stability of γ - Al_2O_3 and other useful transition aluminas. Stabilization of transitional aluminas can take place via delaying the nucleation of stable alpha-alumina. This is possible if the particle size of transitional aluminas does not exceed that of the critical nucleus size for the alpha- Al_2O_3 (sintering) and if no nucleation sites for nucleating alpha- Al_2O_3 . Generally, some additives or modifiers are used to prevent or delay the alumina transformations. These additives can act by reducing sintering, reducing the number of nucleation sites or increasing the nucleation activation energy. These additives include rare earth oxides, alkaline earth

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oxides, silica, transitional metal oxides and other oxides [4–17]. However there are poor data concerning the thermal stabilization of γ - Al_2O_3 utilizing strontium as a stabilizer. In this study the effect of SrO addition on the stabilization of transition aluminas and its improving effect in the preparation of alumina membranes will be discussed.

2. Experimental

Aluminum chloride hexa-hydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, Merck) and strontium nitrate ($\text{Sr}(\text{NO}_3)_2$, Merck) were used as starting materials. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in distilled water and the pH of resulting solution was adjusted to 3.0. Ammonia solution (NH_3 , Merck) was added as a precipitating agent into the solution and the pH of the solution was adjusted to 7, 8 and 9 and the solution stirred with a magnetic stirrer. After aging the precipitate for about 5 min, it was filtered and washed with distilled water until Cl^- ions could not be detected by 1 M of AgNO_3 solution. The filtered powders prepared at various pH conditions were dried in oven at 110°C for 24 h. Proper amounts of the obtained wet cakes was poured in a beaker and diluted by adding water to gain a 10 wt.% Al_2O_3 boehmite suspension. Diluted nitric acid solution (HNO_3 , Merck) with a normality of 2 was used to peptize the suspension for the production of a sol. The initial pH of suspension (pH \sim 5) was reduced gradually and adjusted to 3–3.5 by adding HNO_3 solution. During peptization, removal of agglomerates from the suspension takes place which eventually results in a clear sol.

After addition of some PVA solution into the sols (for avoiding crack formation during drying at later stages) the sol was submitted to ultrasound treatment for 15 min. After the determination of the optimum precipitation pH, Al_2O_3 - x wt.% SrO composite powders ($x=1, 3, 5, 8$) were synthesized by dissolving appropriate amounts of $\text{Sr}(\text{NO}_3)_2$ powder to the aforementioned AlCl_3 solution and post-precipitating at a chosen pH and preparing boehmite sols from composite cakes as explained before. After aging for 24 h the prepared sol was used for fabricating supported or unsupported membranes. Disk shaped alpha-alumina supports (15 mm diameter, 2 mm thickness, ca. 40% porosity and $0.2\ \mu\text{m}$ average pore diameter) were obtained from the Materials and Energy Research Center, Tehran, Iran. Supported membranes were prepared by dip-coating the α -alumina supports in the prepared boehmite sols. Before dip-coating, the boehmite sol was mixed with a PVA solution (PVA: boehmite mass ratio of 0.85). PVA was used as drying chemical control additive (DCCA) to prevent crack formation during drying process [20]. Dip-coating time was 15 s. Wet membrane layers were dried at ambient temperature for 24 h. Afterwards they were heat treated at 50°C for 1 h and afterwards at 1100°C for 1 h. In order to prepare unsupported layers, a small amount of sol was poured in a polypropylene Petri-dish and dried at 50°C . Dried unsupported membranes were heat treated at 600, 800, 1000 and 1100°C with a ramping rate of $20^\circ\text{C}/\text{min}$ to maximum temperature and soaking time of 1 h. In any part of the sample preparing procedure, the working temperature was ambient temperature, except for the heat treatment stages.

All dried and calcined unsupported membranes were characterized by X-ray diffraction using a Jeol 8030 diffractometer with $\text{Cu K}\alpha$ radiation in the range of 5 – 80° . In order to gain further insight into the phase-transformation behavior of the alumina phases, the phase transformation temperatures of the different samples were measured by means of Simultaneous Thermal Analysis (Shimadzu-449C). About 20 mg of powdered samples was heated up to 1350°C at a rate of $10^\circ\text{C}/\text{min}$ in air atmosphere. Scanning electron microscopy (Philips XL30) was used to examine surfaces and cross-sections of the supports, supported membranes and the microstructural evolution of the unsupported membranes.

The cross-sectional samples were cast in resin and polished before examination. In order to follow the evolution of the membrane pore size and specific surface area when exposed to higher temperatures, BET surface areas and adsorption isotherms of the unsupported membranes were determined using a Micromeritics (Gemini 2375 V4.02) apparatus. Nitrogen gas was used with relative pressures ranging from 0.05 to 0.99 to adsorb within the pores. The pore size distribution of the unsupported membranes was calculated using the BJH method based on the adsorption isotherm [18].

3. Results and discussion

Fig. 1 shows the XRD patterns of the dried powders of the initial wet cakes prepared under different pH's. As the pH value increases from 7 to 9, the phases of obtained aluminum hydroxides changes from amorphous to boehmite (AlOOH), bayerite ($\text{Al}(\text{OH})_3$) and nortstrandite ($\text{Al}(\text{OH})_3$). This trend may be attributed to an increased amount of OH^- ions from added NH_4OH [19]. Alumina has many transitional phases. Each of them can be derived from an initial aluminum hydroxide phase upon proper heat treatment. The starting hydroxide has a great influence on the type of transition aluminas and the temperature of any phase transformation. From a catalytic point of view, boehmite is among the best candidates as a starting hydroxide phase and has a relatively high specific surface area. Boehmite transforms sequentially into gamma (γ - Al_2O_3), delta (δ - Al_2O_3) and theta (θ - Al_2O_3) and alpha phases upon heat treatment. Any of these transitional phases has a relatively high specific surface area and has desired catalytic activity. However there is some difference in specific surface area of these phases. In order to gain boehmite phase, the pH value of the solution was optimized at 8. Fig. 2 shows the XRD patterns of the powdered unsupported membranes at 1100°C containing various amounts of SrO dopant. As can be seen from Fig. 2, composite powders with SrO content lower than 5 wt.% SrO were transformed to alpha-alumina after calcination at 1100°C . On the other hand, addition of 5 and 8 wt.% SrO stabilized delta and theta transitional aluminas although some residual alpha phase was present in small quantities. Stability coefficient of transitional alumina phases with respect to alpha-alumina was greater in the powder containing 5 wt.% SrO. Fig. 3 shows the XRD patterns of the powders containing 5 wt.% SrO calcined at different temperatures. Dried powder initially consisted of boehmite which transformed mostly to γ - Al_2O_3 at 600°C . The γ - Al_2O_3 phase persisted at 800°C . After calcination at 1000°C , a mixture of δ - Al_2O_3 and θ - Al_2O_3 could be identified. At 1100°C , samples with an SrO content lower than 5 wt.% transformed completely to α - Al_2O_3 and the sample containing 5 wt.% SrO into a mixture of δ - Al_2O_3 , θ - Al_2O_3 , and α - Al_2O_3 phases. Calcination at

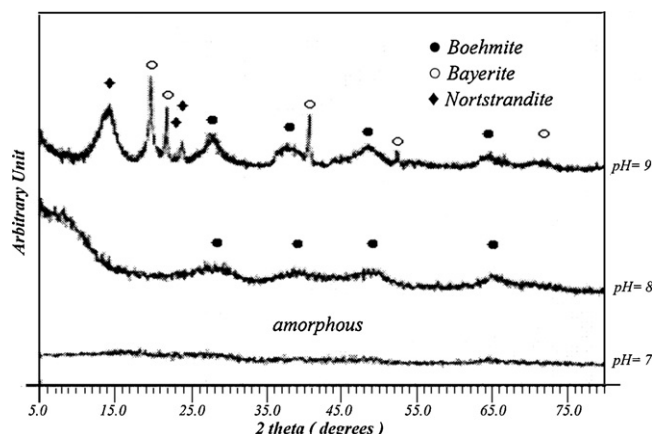


Fig. 1. Dependence of aluminum hydroxides to pH of the precipitation.

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