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Effect of catalyst used in the sol–gel process on the microstructure and adsorption/desorption performance of silica aerogels

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ABSTRACT

Silica aerogels prepared by the sol–gel process are often used as solid desiccants in enthalpy wheels for dehumidifying ventilation air in air-conditioning systems. These hygroscopic materials have good moisture adsorption and desorption characteristics due to their porous structure. The current study is focused on the evaluation of the mass diffusivity of silica aerogels, which determines the rate at which a dehumidification process can be performed. The mass diffusivity of silica aerogels is affected by their porous structure which depends on the synthesis technique used to prepare the silica aerogels. The sol–gel process is used to prepared silica aerogels using various basic (ammonium hydroxide, sodium hydroxide, potassium hydroxide) and acidic (hydrofluoric acid, steric acid, hydrogen peroxide) catalysts with the same precipitator (tetramethyl orthosilicate – TMOS) and solvent (methanol). Scanning electron microscopy is used to analyze the microstructure of supercritically dried aerogels. The dynamic vapor sorption method is used to determine the effective mass diffusivity for the different silica aerogels. It is found that the mass diffusivity is related to the microstructure of silica aerogels, which depends on the catalysts used in the sol–gel process. In addition, a parametric study is conducted to determine the effect of relative humidity and temperature on the adsorption and desorption mass diffusivity.

1. Introduction

Most recent studies of dehumidification systems have focused on the development and application of solid adsorbent materials that can provide improved adsorption capacity and higher moisture adsorption/desorption rates [1–3]. Adsorption systems with improved performance promise considerable savings in operating costs and in some cases make such dehumidification systems attractive alternatives to existing vapor compression systems for cooling and dehumidification. Generally, solid salt adsorbents (e.g. calcium chloride and cobalt chloride) have greater hygroscopic capacity than other inorganic adsorbents, such as silica gel; however; calcium chloride granules often deliquesce beyond an adsorptive capacity of 0.33 kg/kg, after the formation of the solid crystalline hydrate, $CaCl_2\,2H_2O$ [3]. In order to overcome this problem, desiccant materials based on silica gel have become attractive alternatives to the salt-based adsorbents. They have been used as high-performance desiccants to remove water vapor from humid ventilation air for buildings [4]. Silica aerogels are highly porous materials with low density, low thermal conductivity, and large surface area. They have received significant attention in heat insulation [5], waste treatment [6], drug delivery and targeting systems [7,8] as well as many other applications. Silica aerogel has a relatively high moisture adsorption capacity because of its microporous structure of internal interlocking cavities, which gives a high internal surface area (up to 800 m^2/g, or 10^8–10^9 m^2/m^3) [9]. When the water vapor pressure at or near any pore region of a silica gel particle is lower than the surrounding water vapor pressure, water molecules diffuse through the air to the surface and adhere to the surfaces, especially the internal surface of the silica gel. The higher the humidity of the air, then the greater the mass of the water adsorbed by the silica gel. An advantage of using silica aerogel is that there is no chemical reaction during adsorption, unlike many salt absorbents which change their chemical composition and physical appearance with the addition of water. Even when saturated with water, silica gel still has a dry appearance with its geometry unchanged. The adsorption and desorption characteristics of different silica gel samples may vary because of different manufacturing procedures [3]. Although silica gel is frequently used as a desiccant, heat and moisture transport within the pores of silica gel particles are complicated processes and

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Nomenclature

a	radius of the silica aerogel block (mm)	t	time (s)
D	effective diffusion coefficient (m^2/s)	ρ	moisture density (kg/m^3)
L	length of the block (mm)		

research is ongoing. Comprehensive experimental studies of the physicochemical properties and some research applications of the organic and salt-based adsorbents have been reported by Aristov et al. [1] and Zhang et al. [3]. These studies show that silica-aerogel-based adsorbents have a higher adsorption capacity and can be regenerated with a lower temperature than other commercially available desiccants, such as activated carbon. Despite such promising properties, conclusions as to the feasibility of these materials for sorption systems can only be drawn after dynamic analysis of the absorbent and desorbing performance under operating conditions typical to sorption/desorption systems. The performance of a porous adsorbent solid is determined not only by the adsorption isotherm, but also by the desiccant mass diffusivity, which affects the adsorption rate. Many researchers have evaluated the dynamic adsorption properties such moisture diffusion coefficients of silica aerogels in general. However, most of such studies have assigned one specific diffusivity to all silica aerogels without realizing that some silica aerogels can have completely different microstructure than others depending on the manufacturing methods. Hence to date, rare literature is available about characterizing silica aerogels based on their microstructure and relating it to their effective mass diffusivity. In order to help fill this gap, the main aim of the present work is to investigate the microstructure and mass diffusivity of silica aerogels manufactured using different methods (catalysts in sol–gel process).

2. Literature review

2.1. Preparation of aerogel

Generally, the synthesis of silica aerogels using silicon alkoxide takes place in two steps: (1) a sol–gel process to prepare the gel, and (2) supercritical drying of the gel to obtain an aerogel [10–15]. In a sol–gel process the hydrolysis of silicon alkoxides generates intermediate species and these species then undergo a stepwise poly-condensation reaction to form a three-dimensional gel network. The secondary step is the supercritical drying of the gel, which involves drying at the critical temperature and pressure of the solvent present in the pores of gel to form an aerogel. The supercritical drying for the synthesis of silica aerogels requires a special type of autoclave assembly. Many research groups have synthesized silica aerogels using tetraethoxy silane precursor (TEOS) using ambient-pressure drying, in which surface chemical modification of silica surface is carried out prior to drying [16–19]. However, silica aerogels prepared using TEOS precursors have the disadvantages of relatively high density and low porosity, which hinders wider application of these materials. It has been observed that in a system with a highly polar solvent, the solvent affects the rate determining step and, therefore, the nature and size of the resulting polymeric particles [20]. It has been reported that acetonitrile is a highly polar aprotic solvent which does not form hydrogen bonds with the silicate nucleophile but reduces the rate of the condensation reaction. This behavior is due to the high polarity of acetonitrile, which stabilizes the anionic reactants with respect to the activated complex [21]. Furthermore, acetonitrile is an easily displaceable ligand and miscible with water and methanol. Therefore, in order to obtain optically transparent and low density silica aerogels, acetonitrile has been employed in the sol–gel process [22,23]. However, in these reports the methods used for the preparation of aerogels are time consuming and not scalable for commercialization.

Brinker and Scherer [24] described the parameters that affect the sol–gel process including the way hydrolysis and condensation are carried out, the pH of the catalyst used, and the temperature and pressure. Their work also described the effects of ageing and possible applications of different types of aerogels. Prakash et al. [25] prepared silica films with the range of porosity from 91% to 98.5% at ambient pressure by a process wherein organo-siloxane polymers were deposited on a silicon substrate by conventional dip-coating at 25 °C and 0.85 bar, and then heated to 450 °C. The film thicknesses varied from 0.1 to 3.5 μm, depending upon the dip-coating rate (0.05–1.9 cm/s) and concentration of the solvent. The process was optimized by varying the dilution, ageing, organic modification, heat treatment and dip-coating conditions, allowing control of film porosity from 30% to 99%. Scherer et al. [26] found that when a gel is heated, the thermal expansion of the pore liquid causes stretching of the solid network. If the heating rate is very high, the gel expands at the same rate as the liquid; at slower rates, some of the liquid drains out and the gel expands less. Pel et al. [27] presented a procedure to determine the moisture diffusivity for drying from measured moisture concentration profiles. They also described a means of determining the relative error of moisture diffusivity, when they used their proposed method for evaluating diffusion performance.

2.2. Characterization of aerogels

Shen et al. [28] prepared silica aerogels by a sol–gel technique from industrial silicon derivatives (polyethoxydisiloxanes, E-40), followed by silylation and drying under ambient pressure. The specific surface area, pore size distribution and thermal conductivity of the silica aerogels were investigated and the results showed that the diameter of the silica particles was approximately 6 nm, and the average pore size of the silica aerogels was 14.7 nm. The specific surface area was approximately 1000 m^2/g and the thermal conductivity was approximately 0.014 W/m-K at room temperature and a pressure of 101 k Pa. Si—CH_3 groups were also detected on the surface of the silica aerogels, which explained the hydrophobic behavior of silica aerogels. Lucas et al. [29] analyzed pore structures and mechanical properties of silica aerogels obtained by traditional base-catalyzed sol–gel synthesis. They concluded that these characteristics can be modified by curing in neat methanol. The curing process produced gels with a larger mean pore-size and more cumulative pore volume than their uncured (standard) counterparts, both before and after heat-treatment steps. Cured silica aerogels that were densified by heat treating in air at 900 °C for 30 min retained a mean pore-size of about 30 nm, comparable to a standard or dry silica aerogel. Heating the standard silica aerogel to 900 °C for 30 min markedly decreased the mean pore-size to 16 nm.

Yadav and Bajpai [30] analyzed the regeneration and adsorption performance of different desiccants, such as silica gel, activated alumina, and activated charcoal, for producing dry air. The air needed for regeneration was heated in an evacuated-tube solar