Surface fractal study of perovskite alumina ceramic membrane prepared by sol-gel method from adsorption isotherm description

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Abstract

Perovskite alumina membrane has been synthesized by the sol-gel method. The molar ratio of alkoxide to water and acid 1 100·0 07 was used to prepare the sol Observation were made on pore size and BET surface area at different temperature using N_2 sorption analysis. The average pore size increased with the increasing of temperature Pore surface roughness changes in perovskite-alumina membrane have been investigated by surface fractal dimension analysis The Frenkel-Halsey-Hill (FHH) model for multilayer adsorption was applied to obtain the surface fractal dimension Surface fractal dimension increases while calcined from 400°C to 600°C but decreases at temperature 800°C. SEM analysis observed the surface morphology of the membrane.

Keywords: Alumina membrane, perovskite, sol-gel, pore structure, surface fractal dimension.

Introduction

The potential of inorganic membranes such as alumina ceramic membranes in separation process have been recognized for a long time due to its high thermal, chemical and mechanical stability at elevated temperature Several methods have been developed

1

for the characterization of porous membranes. N_2 adsorption/desorption is the simplest technique to obtain the pore characteristic such as pore size, BET surface area and pore size distribution However, additional information such as fractal geometry can be extracted [1]

Fractal geometry has been demonstrated to be a very useful method in many areas of science and engineering since it was introduced by Mandelbrot in 1970s [2] Fractal geometry suggests that at the molecular size range, the surfaces of most materials are fractals Among the different ways to define fractal geometry, the term surface fractal has been used to identify the fractal dimension, D The surface fractal dimension, D, is a global measure of a surface irregularity for variety of materials such as carbon particles, gold films and silica gels [3] The D value should lie in the range of 2<D<3 depending on the degree of irregularity. The D value near 2 indicated the perfectly smooth surfaces The D value increases with the degree of surface irregularity At a D value close to 3, the surface is very rough and irregular Therefore, the D value can be considered as an operative measure of the surface roughness [4,5]

There are several ways to evaluate the D value from adsorption data such as Frenkel-Halsey-Hill (FHH) method, thermodynamic method and Pfeifer-Avnir method Among this method, FHH model is the most popular method to determine the surface fractal dimension from N_2 adsorption measurement The FHH model for multilayer adsorption is described by the following equation

$$\frac{N}{N_m} = k\left[\ln\frac{P_o}{P}\right]^{D-3} \tag{1}$$

where N/N_m is the number of layers adsorb on the surface, k is a constant, P and P_o are the equilibrium and saturation pressure of nitrogen adsorbed D is surface fractal

dimension. The value of N_m can be obtained from the BET model The surface fractal dimension can be calculated from the slope of a plot of $ln(N/Nm)$ versus $ln[ln(P_o/P)]$

The present study investigates the surface fractal dimension, D of perovskite alumina membrane and the effect of temperature on surface irregularities. Usually, the surface roughness was observed using SEM analysis In this study, the effect of temperature on surface roughness and irregularity was obtained from calculation. The membranes roughness was determined in the range of 400°C to 900°C.

Experimental method

The perovskite doped in alumina sols were prepared using sol-gel technique. One mole of $Al(OC_4H_9)_3$ was hydrolyzed in 100 mol of distilled water at 90°C and stirred for 30 minutes to achieve complete hydrolysis. Then, HNO_3 with a molar ratio of 0.07 of H^+ to Al^{3+} was added to peptize the sol followed by the addition of aqueous solution of perovskite doping element. The solution was stirred for 30 minutes then kept under reflux condition for 20 hours at 90°C to ensure complete mixing and hydrolysis PVA was used as a binder to prevent crack formation at initial drying process and was added in the initial solution during a 20 hours reflux condition. The perovskite doped alumina gel was prepared by pouring 3 ml of sol in Petri dish and dried for 24 hours under ambient conditions The gels were calcined at the range of 400°C to 900°C to get the unsupported membranes. The supported membranes were prepared by dip-coating the alumina disk support in perovskite doped alumina sol and dried under ambient temperature for 24 hours. After drying, the samples were calcined. Alumina disk support was prepared by pressing the alumina powder with particle size of 45μm into a disk

shape with diameter 20mm and 2mm thickness. Alumina disk was dried and sintered at 1000°C.

N_2 adsorption/desorption isotherm measurements were performed to determine the pore characteristic of the perovskite alumina membrane. The measurements were carried out on unsupported membranes top layers assuming that the properties were similar to those of supported membrane layers [6] Scanning electron microscope was used to characterize the surface morphology of supported membrane.

Result and discussion

The pore characteristic of perovskite alumina membrane calcined at different temperature is shown in Figure 1 As can be seen, there is a gradual decrease in the surface area with the increasing of temperature At 400°C, the BET surface area was 340 8 m^2/g, after the temperature was increased to 900°C, the surface area was reduced to 187 5 m^2/g. The loss of specific area is due to the elimination of water from surface hydroxyl groups and will result in new Al-O-Al bonds with a decrease of the surface area [7]. The pore size of membrane increased with increasing of temperature It indicates that much more coarse pores have been developed in the membrane at higher temperature than at lower temperature [6]. The pore size increased from 3 88 nm to 6.80 nm when temperature was increased from 400°C to 900°C

The adsorption/desorption isotherm of perovskite alumina sintering at different temperature are shown in Figure 2 The shape of isotherm was characterized as Type IV, which confirmed the fine mesoporous characteristic of perovskite alumina membrane

materials at temperature range of 400°C to 800°C. At 900°C, the isotherm was characterized as Type II indicating the presence of larger macropores [6]
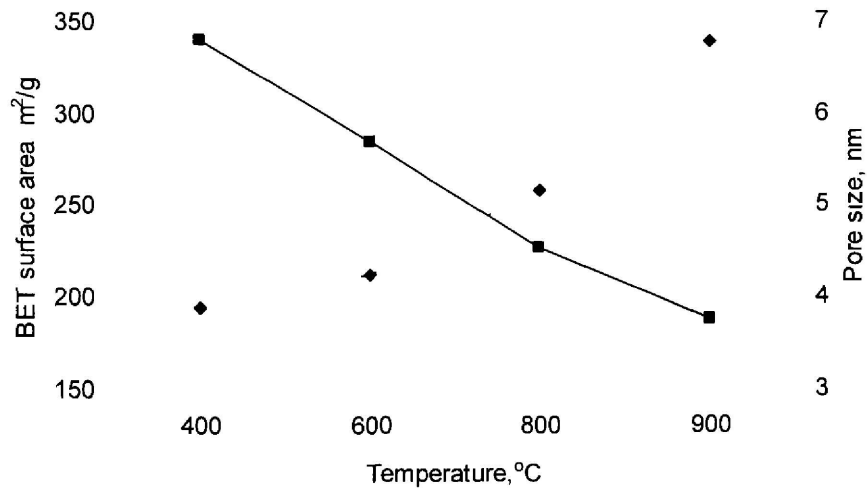

Figure 1   The effect of temperature on BET surface area and pore size
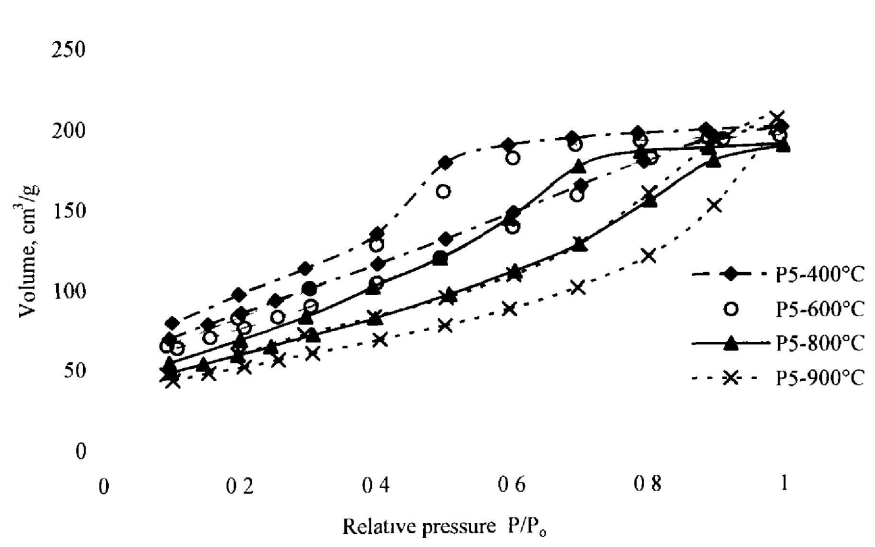

Figure 2   N₂ adsorption/desorption isotherm of perovskite alumina membrane calcined at different temperature.

The adsorption data are plotted according to equation 1 Figure 3 shows the plot of $ln\ N/N_m$ versus $ln[ln(P_o/P)]$ The surface fractal dimension, D, values was obtained from the slope of the linear plots and listed in Table 1 It can be seen that, the D value is in the range of 2<D<3 The surface fractal of membrane increased when the temperature was increased from 400°C to 600°C The calcinations process induces a restructuring phenomenon and results in the increase of the fractal dimension of membrane clusters The surface roughness of membrane increases as the surface fractal dimension increases [3] Nevertheless, it was noted that at 800°C the surface fractal showed a slight decrease The deformation mechanism of the pore size will occur as the temperature increase The driving force of calcinations process will transform the areas with large convex curvature to areas with small convex curvature The clusters will become smoother and have lower fractal dimension. Pores located between clusters will collapse because clusters are "swallowed" by larger ones [5] The broadening of pores, surface smoothing and calcinations effect also contributed to the decreases of surface fractal dimension at higher temperature [8] The increasing of surface fractal dimension at 900°C might result from the increase of surface textural complexity due to calcinations Similar trend was reported by Huang et al , (2001)
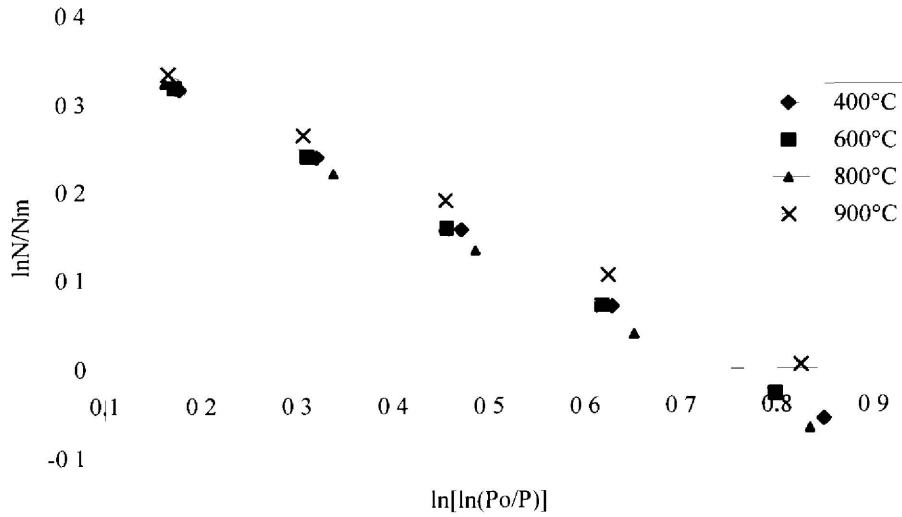
0 4

0 3

0 2

lnN/Nm

0 1

0

-0 1

0,1   0 2   0 3   0 4   0 5   0 6   0 7   0.8   0 9

◆   400°C
■   600°C
▲   800°C
✕   900°C

ln[ln(Po/P)]

Figure 3   Plots of *ln N/N_m* versus *ln[ln(P_o/P)]* of perovskite alumina membrane at different temperature.

Table 1   Surface fractal dimension of perovskite alumina membrane calcined at different temperature.

Samples	Temperature, °C	Surface fractal dimension, D
		FHH model
Perovskite	400°C	2 443
alumina	600°C	2 445
membrane	800°C	2.425
	900°C	2 488

The surface morphology of perovskite alumina membrane calcined at 400°C and 900°C are shown in Figure 4 (a) and (b). The surface of perovskite alumina membrane calcined at 900°C is very rough when compared to at 400°C It shows that, the roughness of membrane observed using SEM observation is consistence with the surface fractal dimension calculated using FHH model
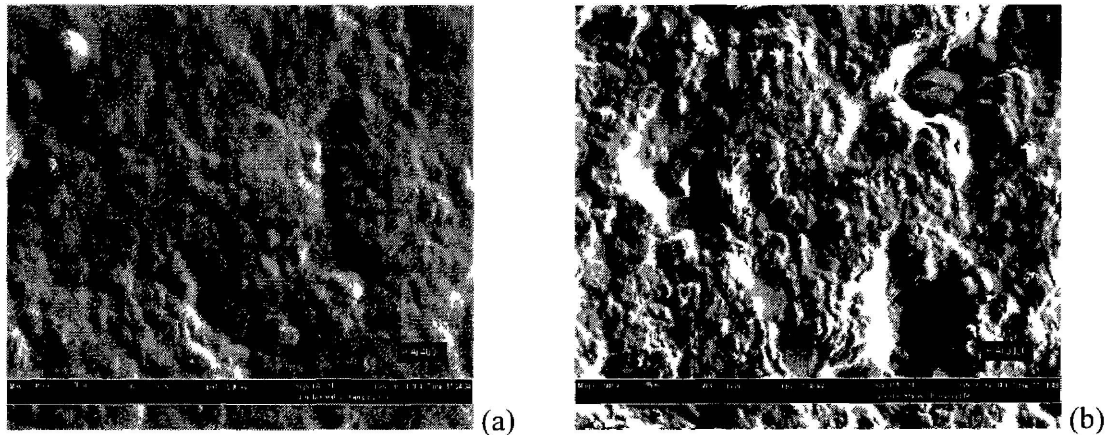
Figure 4   Surface morphology of perovskite alumina membrane calcined at
(a) 400°C and (b) 900°C

Conclusion

The effect of temperature on pore size and surface fractal dimension of perovskite

alumina membrane was studied. The pore size of the membrane increased with the

increasing of calcinations temperature The perovskite alumina membranes have rough

surfaces and the value of surface fractal dimension, D is in the range of 2 to 3 The

surface fractal dimension increased slightly when the calcinations temperature was

increased from 400°C to 600°C The decreased of surface fractal dimension had occurred

due to broadening of pores, surface smoothing and calcinations effect at 800°C

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