Influence of Calcination Temperature on Microstructure and Surface Charge of Membrane Top Layers Composed of Zirconia Nanoparticles

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Abstract

The purpose of the research is to investigate the changes in microstructure and physicochemical characteristics, mainly surface charge (i.e. zeta potential) of zirconia membrane top layer during calcination. Zirconia is one of the most commonly preferred materials for ceramic membrane top layers due to its superior durability. The physicochemical properties of the top layer composed of submicron / nano particles is necessary not only for Donnan exclusion but also for dynamics of membrane fouling. In the present research the possibility of preparation of zirconia top layers with varying surface charge with changing calcination temperature was shown and a correlation between phase transformation and surface charge was determined.

Keywords: zirconia, membranes, sol-gel, calcination, zeta potential

INTRODUCTION

Zirconia is one of the oxides widely used in preparation of top layers of multilayer ceramic composite membranes due to its relatively high chemical stability [1], in a wide pH range [2], especially in alkaline high pH media [3]. It is also preferred for various applications like thermal barrier coatings, electrolytes and anodes in solid oxide fuel cells, gas sensors, gate dielectrics, biomaterials, etc. [4, 5, 6]. Amphoteric character of zirconia with its high thermal, mechanical and chemical stability makes zirconia a promising catalyst and catalyst support [7, 8]. Therefore it is used as catalyst support and as a catalyst in different catalytic applications e.g. reduction and hydrogenation reactions [9], methane combustion, CO oxidation and low temperature liquid phase cumene oxidation [8] and photocatalytic reactions like decomposition of organic pollutants [10]. Zirconia possesses ion exchange selectivities; both anionic and cationic exchange characteristics [7], oxidizing and reducing surface properties [8]. This characteristic of the zirconia surface is both dependent on medium pH and pre-treatments [7].

The surface characteristic of zirconia is an important parameter for membrane applications as it is for different applications of zirconia. The surface charge of the selective top layer is effective on both fouling mechanism and separation kinetics of the membrane. A membrane with similar surface charge with the particles to be filtered may be more prone to fouling. Besides the surface charge of the membrane may be determining on filtration of charged species as the pore size of the membrane decreases, like in ultra- or nanofiltration. This phenomenon explained by Donnan exclusion mechanism is sometimes more effective than size exclusion mechanism which is related to the physical screening of species with respect to their mass and the pore size. Shang, *et al.*, reported the phosphate rejection of the ceramic membrane with 3kDa MWCO (molecular weight cut-off) was greater than the 1 kDa membrane since the former has a greater negative surface charge [11]. Therefore, both the microstructure and the surface characteristics of the membranes are important for separation efficiency in filtration applications (especially ultra- and nanofiltration).

The sol-gel method enables preparation of fine colloidal precursor sols, which form porous membrane layers after drying and heat treatment [12]. The size of the particles in the sol is important since these particles will collide and form the microstructure after drying and heat treatment. The coating of the sol and its oxidation should be performed appropriately to prepare membranes with desired microstructure and surface characteristics. The heat treatment ensures the

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physical stability of the membrane layer against peeling under flow during filtration applications. It is also effective on final microstructure (i.e. the size and distribution of pores) of the membrane formed [13]. The parameters during heat treatment should be selected appropriately to preserve the porous characteristics of the membrane layer and prevent excessive sintering.

The influence of the calcination temperature on the surface charge of zirconia membrane layers in a temperature range selected to preserve porous microstructure was investigated in this work. For this purpose unsupported membrane layers were prepared for characterization tests like surface charge determination and XRD analysis.

EXPERIMENTAL

Polymeric zirconia sol was prepared by using zirconium propoxide, propanol, nitric acid and water with molar ratios of 1:13.31:0.826:2 as reported previously [12, 14]. The zirconium propoxide was 70 wt. % solution in propanol, the other chemicals were reagent grade. The sol was prepared by the addition of a solution containing nitric acid, water and a fraction of the necessary propanol to the propanol alkoxide mixture drop-wise. The particle size distributions of the sols were determined by using a laser light scattering instrument (Zetasizer 3000HSA, Malvern, Co., UK). The polymeric sols were poured into Petri dishes and dried at room temperature overnight to prepare unsupported layers / membranes. Thermogravimetric analysis (TGA) was conducted for the determination of the thermal behaviour of the dried unsupported layers / membranes by using a heating rate of 10°C/minute. The dried unsupported membrane samples were calcined at different temperatures in a furnace (Carbolite CWF1300). The heating rate was 5°C/minute and the samples were kept at dwelling temperatures for 150 minutes. The calcined powders were characterized by using X-ray diffraction (XRD, CuKα, Philips Expert Pro) and scanning electron microscope (SEM, Philips XL30 SFEG). Calcined powders were dispersed in potassium chloride solution (10^{-3} M KCl) with an initial pH of 7.4 in an ultrasonic bath for dilute stable suspension preparation. Zeta potentials were determined by using a laser light scattering electrophoresis instrument with at least 3 repetitive measurements (Zetasizer 3000HSA, Malvern, Co., UK).

RESULTS AND DISCUSSION

The volumetric particle size distribution of the zirconia sol is shown in Fig. 1. The average particle size of the sol was 4.9 (± 0.4) nm with a polydispersity index (PI) of 0.534 (± 0.051), indicating a homogeneous particle size in a few nm range. The thermogravimetric analysis (TGA) result showing the weight loss behaviour of the room temperature dried zirconia sol as a function of temperature is given in Fig. 2. There were weight losses probably due to the removal of bound water (room temperature – 150 °C) and removal of organic constituents (150 - 400 °C) at temperatures lower than 400°C. There was also an additional weight loss of about 5 % in the 400-500°C range and the sample was thermally stable after 500°C. The temperature range of 400-500° C was further selected in order to investigate the effect of heat treatment on the surface properties of the membrane.

The SEM micrographs of the unsupported membranes calcined at different temperatures are shown in Fig. 3. The presence of a network of nanoparticles with sizes around 15-40 nm for all calcination temperatures is visible in the micrographs. A stable microstructure without loss of porous structure due to over-sintering was maintained in the calcination temperature range investigated. Similar observation on the stability of the microstructure was reported based on the TEM analysis of zirconia heat treated in the 300 - 600°C for 2 h in a previous study [15].

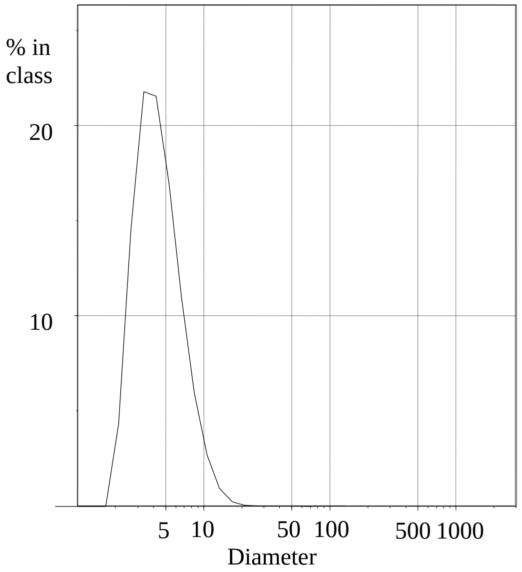

Fig. 1: The volumetric particle size distribution of the sol determined via laser light scattering instrument

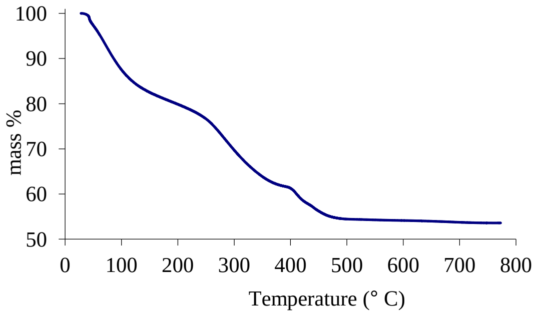

Fig. 2: The thermogravimetric (TGA) behaviour of the room temperature dried zirconia sol

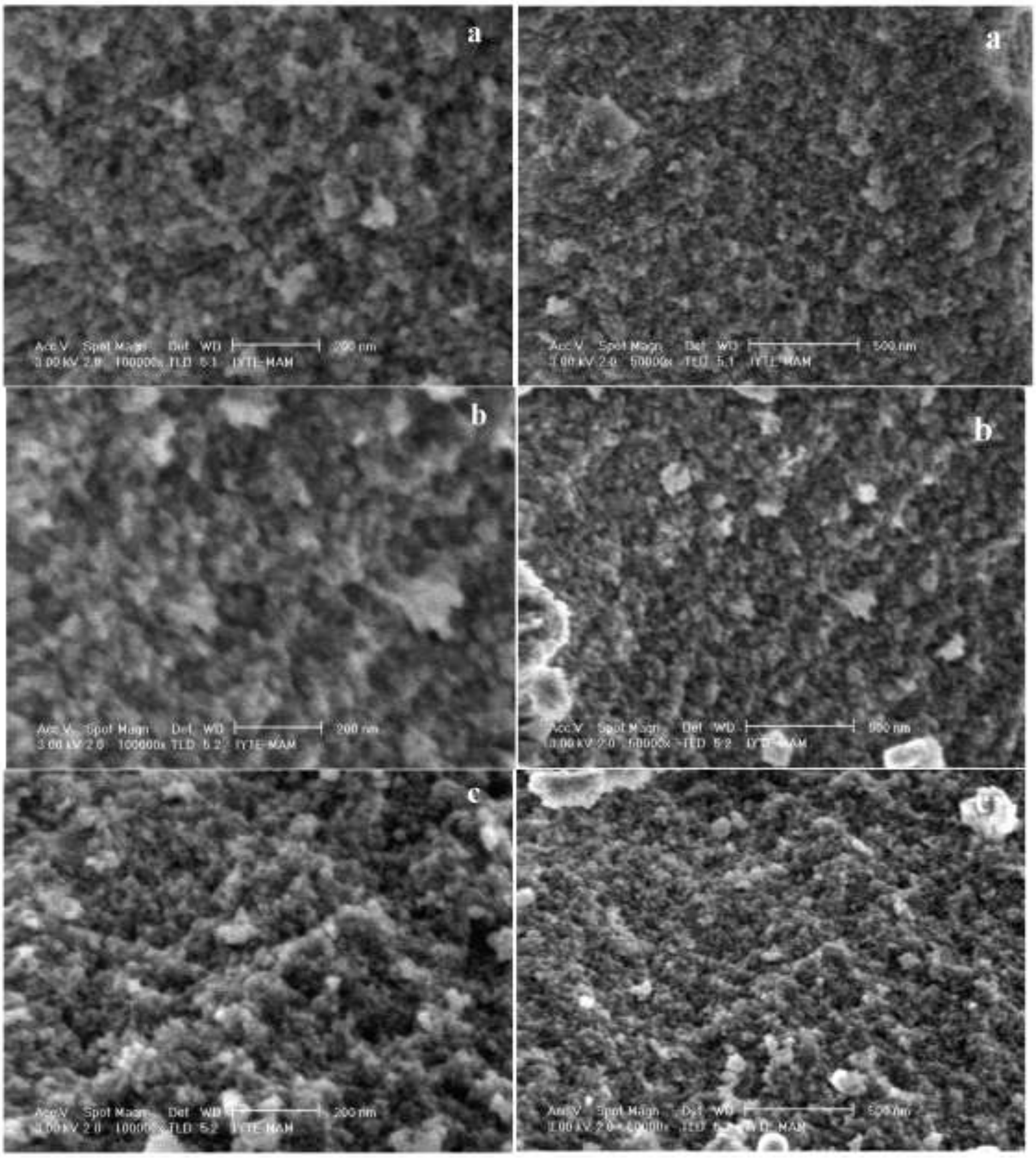

Fig. 3: The SEM micrographs of the samples calcined at 400° (a), 450° (b) and 500° C (c) at two different magnifications (the scale bar is 200 nm and 500 nm for micrographs on the left and on the right, respectively)

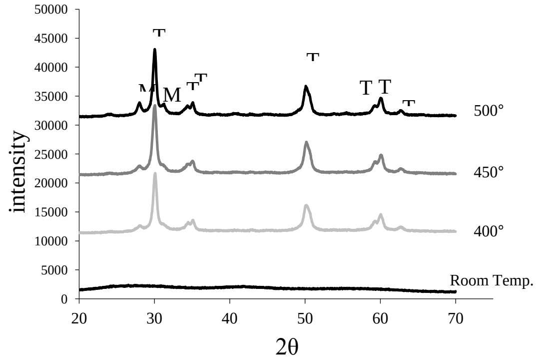

Fig. 4: The XRD patterns for zirconia powders calcined at three different temperatures (M: monoclinic, T: tetragonal)

Zirconia has a polymorphic structure in the temperature range investigated. X-ray diffraction (XRD) results indicated the tetragonal phase as the dominant phase in the calcined zirconia samples at three different temperatures as shown in Figure 4. The intensities of the peaks indicating the presence of monoclinic phase increase as the calcination temperature increases. Benfer *et al.* [16] reported that ZrO_2 prepared with diethanolamine as a hydrolysis - condensation reaction regulator in sol preparation was in metastable tetragonal phase after calcination at 500°C and there were no peaks for monoclinic phase in the XRD patterns of that sample. Van Gestel *et al.* [2] prepared zirconia sols with acetylacetone to prevent rapid hydrolsis-condensation reactions. They calcined the unsupported layer formed by this sol at 400 and 450°C. The XRD patterns indicated the presence of monoclinic phase in the sample calcined at 450°C. In our samples ratio of monoclinic phase increased with increasing calcination temperature with respect to the intensity of XRD peaks as shown in Fig. 4.

The zeta potential values of dispersions of zirconia calcined at different temperatures are shown in Fig. 5. The zeta potential values in magnitude increased linearly (~32%) in the 400-500°C range. A similar increase in zeta potential values with increasing calcination temperature was also reported by Prica *et al.* [17]. In that research, the magnitude of zeta potential of zirconia was around -15 and -25 mV in 10^{-3} M KNO_3 solution at pH 7 for samples heat treated at 450° and 650°C, respectively [17]. The final pH values of the dispersions were only slightly higher than the initial pH (7.4) of the solution before zirconia addition as can be seen in Figure 5. The variation of the zeta potential values was determined to be in correlation with the XRD results i.e. increasing monoclinic phase content of the unsupported membrane.

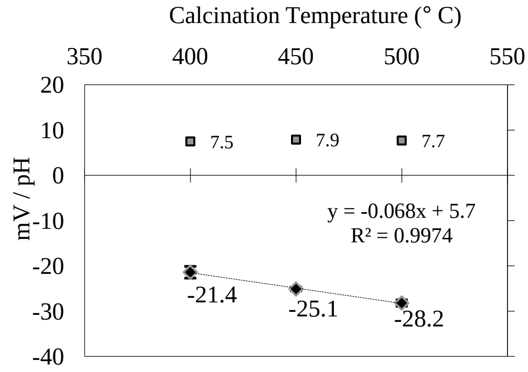

Fig. 5: The zeta potential of the unsupported zirconia membrane dispersed in 10^{-3} M KCl solution with initial pH value of 7.4 and the final pH values of the solution

These differences in the zeta potential values of samples calcined at different temperatures indicate the possibility of the preparation of membrane layers and coatings with different surface characteristics, which may be used for different separation processes and other applications.

Zirconia calcined in the temperature range investigated presents polymorphic structure. The ratios of different morphologies (phases) in this structure possibly determine the surface characteristics. The differences in the zeta potential values (~32% in magnitude) are promising to prepare ceramic membrane layers with different surface characteristics while preserving a stable pore structure during heat treatment. The differences in the zeta potential values of porous zirconia structure may be appreciated by different scientific applications like preparation / modification of choromotographic analysis and separation methods. The catalytic activities of these unsupported layers with different surface characteristics should also be investigated, since it was reported that the preparation procedure affect the phase change and consequently catalytic activity of zirconia e.g. on esterification reaction for biodiesel production [10, 18].

CONCLUSION

Zirconia is a widely preferred ceramic for different applications. For membrane processes both the surface charge and microstructure of the membrane top layer are important, since they are effective on Donnan exclusion and size exclusion mechanisms, respectively. In this work, possibility of preparation of ceramic membrane top layers with appropriate porous structure with varying surface charge (zeta potential) values was presented. A correlation between the varying zeta potential and zirconia phase transformation from tetragonal to monoclinic phase was observed. These results may be beneficial for preparation of tailor-made membrane layers or catalysts.

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