



CHAPTER V

PREPARATION OF ZIRCONIA POWDERS BY SOL-GEL ROUTE OF SODIUM GLYCOZIRCONATE COMPLEX

Abstract

Zirconia powders were prepared by a sol-gel method, using sodium glycozirconate complex as precursor synthesized via the Oxide One Pot Synthesis (OOPS) process. Gelation of this precursor was achieved through the variation of the hydrolysis ratio without the use of the dopants. The gel samples were also calcined at different temperatures. The resulting zirconia was characterized using X-ray diffraction and nitrogen adsorption/desorption. The solid materials obtained after heat treatment at 500°C by varying the hydrolysis ratio have large surface areas of 154-220 m² g⁻¹ and a narrow pore size distribution in the mesopore region. By variation of the heat treatment, the zirconia xerogels existed in either an amorphous, tetragonal, or monoclinic form at room temperature. Based on XRD data the first identifiable crystalline structure developed from the amorphous phase was the tetragonal polymorph, which was formed between 500 and 800°C. When the temperature is raised to 1000°C, zirconia powder with a monoclinic structure was obtained. Surface areas about 280 m² g⁻¹ was obtained after calcination at 400°C, which drop to ca. 70 m² g⁻¹ following treatment at 1000°C.

Introduction

Recent research interest in zirconia has greatly enhanced the prospects to apply this material in automotive gas sensors, catalysis, etc.¹⁻² However, the properties of zirconia related materials depend on the size, chemical composition of initial zirconia powders. These important properties are controlled by several preparation processes. The sol-gel method is used to obtain ceramic materials exhibiting well-controlled microstructures and better properties than materials prepared by classical procedures.³⁻⁴ Not many studies of aggregation in zirconia based solutions have been done because of the difficulties in avoiding fast hydrolysis of zirconium alkoxide in the presence of even a small amount of water, leading to a fast precipitation of zirconium hydroxide and to heterogeneous gels. Sodium glycozirconate containing ethylene glycolate ligands is alkoxyalkoxide derivative. One advantage of this chelated zirconium alkoxide is hydrolytic resistant, thus resulting in more controllable chemistry.⁵⁻⁷

In this work, zirconia materials were prepared by the sol-gel process of sodium glycozirconate obtained by using the method described in a previous paper.⁸ The goal of this work was to study the preparation of zirconia materials from sodium glycozirconate as a candidate precursor in sol-gel process. Additionally, the effects of processing variables on properties of zirconia calcined at different temperatures were also investigated. The powders obtained were then characterized using BET surface area and XRD after thermal treatment.

Experimental section

Materials. The reagents and preparation of sodium tris(glycozirconate) were those used in previous work.⁸ Zirconium hydroxide was purchased from Aldrich Chemical Co. and used as received. Ethylene glycol was purchased from Farmitalia Carlo Erba and purified by fractional distillation at 200°C, under N₂ before use. Sodium hydroxide was purchased from Merck Company Co. Ltd. and used as received. Methanol and acetonitrile were purchased from Lab-Scan Company Co. Ltd. and purified by standard techniques. Methanol was distilled over magnesium activated with iodine. Acetonitrile was distilled over calcium hydride powder.

The synthesis of sodium tris(glycozirconate) was carried out in one step. A mixture of zirconium hydroxide and sodium hydroxide was suspended in EG, and heated to the boiling point of EG under nitrogen to distill off ethylene glycol along with removal of water liberated from the reaction. The solution was virtually clear, indicating reaction completion. The reaction mixture was cooled down to room temperature and the crude product precipitated out as a white solid. The solid was separated, washed with acetonitrile and dried under vacuum (0.1 mmHg) at room temperature.

Preparation of zirconia materials. The sol-gel process was carried out at 25°C. Sodium glycozirconate was first dissolved in water using different hydrolysis ratio ($h = \text{H}_2\text{O}/\text{alkoxide}$ molar ratio). Hydrolysis ratio ranging from 6 to 24 was investigated. The obtained zirconia based gels were soaked and washed in water to remove the sodium. The separated gel was oven dried at 80°C for 12 h and then calcined at different temperatures. From EDX analysis of the obtained zirconia, it showed that the sodium ion is removed by washing.

Characterization. Simultaneous thermal analysis (STA) was accomplished using a Netzsch STA 409 at a heating rate of 10°C/min. under oxygen atmosphere. This technique was used to investigate the change of gels during the thermal treatment. BET surface area and nitrogen adsorption characterization were performed using an Autosorb-1 gas sorption system (Quantasorb JR.). Test materials were outgassed at 170°C under the reduced pressure, prior to analyses. Powder X-ray diffraction patterns were examined using a RIGAKU RINT 2000 connected with $\text{CuK}\alpha$ source of radiation and operated at 40 kV, 30 mA with Ni filter.

Results and discussion

The thermal behavior of the zirconia gels was studied up to 1000°C using TGA-DTA analyses and XRD. The heat treatment process based on the TG-DTA curves was used to calcine these gels. Figure 1 shows the typical TGA-DTA curves obtained from those dried gels. The weight loss in the temperature range 200-400°C

is due to the combustion of organic species formed by hydrolysis and condensation during the gel preparation. This is supported by the presence of two exothermic peaks at about 200 and 350°C in the DTA curves. It is suggested that elimination of organics through oxidation generates the exothermic reaction. Thus, these peaks were assigned to the oxidative decomposition of organic residues. The first peak is probably due to the evaporation and decomposition of ethylene glycol trapped in the gels and the second peak to those within the pores. An exothermic peak at about 500°C was the result of the decomposition of Zr-OH and some organic residues and crystallization, which was in good agreement with the XRD results. However, at the temperature 500°C, the gel prepared at $h = 12$ exhibits a grayish appearance due to the free carbon remaining in the sample, indicating a need for higher heat treatment temperature. Upon further increasing the temperature, the weight loss in the temperature range 700-800°C was caused by the decomposition of the residual carbon completely removed from a dried gel.

The evolution of the X-ray diffraction patterns of zirconia gels (Fig.2) heated to the desired temperature in the range 400°-1000°C suggests that this exotherm is due to crystallization of amorphous zirconia into the tetragonal phase. Indeed, on heating, a XRD peak at $2\theta = 30.2^\circ$, characteristic of tetragonal zirconia (ICDD file 17-293), was detected. The peak sharpness and intensity increased with temperature indicating an improvement in crystallinity of zirconia. Heat treatment to 1000°C brought about the tetragonal-to-monoclinic transformation. Crystalline phases were identified by comparison with the ICDD file 37-64. In addition, it is worth to note that the crystallinity decreased with increasing hydrolysis ratio. According to the gelation process, when the hydrolysis ratio was increased, the gelation time decreased. The increase in water available for hydrolysis increased the number of Zr-OH groups present. The increase in this group accelerated the condensation reaction, thus decreasing the gelation time. The higher hydrolysis ratio provided less time to arrange itself leading to lower crystallization.

To give the information about the crystallite growth process, representative SEM micrographs of calcined samples are shown in Fig.3. All the micrographs are

exhibited at same magnification. When the calcination temperature is raised, the crystals begin to sinter and agglomerate together affecting the surface areas.

The evolution of the specific surface area as a function of calcination temperature was given in Fig. 4. The surface area decreased when the temperature increased due to sintering. This observation is in agreement with the narrow diffraction peaks, indicating the crystallite growth in the XRD results. An increase of crystallinity followed the reverse trend to the surface area. It is also noted that the smaller the hydrolysis ratio, the lower the surface area. Longer gelation times increased the crystallinity while decreasing the surface area. The general shape of the curves is the same. The BET specific surface area increases with the hydrolysis ratio from 154 to 220 m²/g (Fig. 4). The nitrogen adsorption/desorption isotherm of the zirconia gel for the system with the hydrolysis ratio $h = 24$ and calcination temperature of 500°C was shown in Fig. 5(a). The shape of the isotherm shows the characteristic behavior of the structure of powder, which is composed of an assembly of particles with large open packing. The hysteresis loop in the relative pressure of 0.5-0.9 typically results from wedged-shaped capillaries with a closed edge at the narrow side. According to IUPAC classification, this isotherm shape is of type IV as well as showing a marked hysteresis associated with capillary condensation in the mesopore range (20-500 Å). The hysteresis loop in general matches with type H2. This indicated that the powders contain mesopores. Also, the isotherms show one hysteresis loop, indicating monomodal pore size distributions.⁹ These results suggested that a small pore size distribution and uniform pore structure were obtained. In many applications, the reagent molecules must operate across the porous system, as well as the products have to leave the porous materials. Mass transfer process inside the porous depended on pore size and uniformity of pore structure. Additionally, Fig. 5(b) gave the pore size distribution showing that the mean pore size diameter was approximately 65 Å. Inorganic materials with mesopores of between 2 and 50 nm (according to IUPAC classification) play a role in liquid separations (for example, cleaning of tap water), catalytic materials, carriers and other fields.¹⁰ High area implies fine pores, but relatively small pores, such as < 2 nm, may become plugged in catalyst preparation, especially if high loading are sought. Zirconium oxide powder with a high, thermally stable BET surface area

would be useful for these studies. In all commercial applications, stability of textural properties and resistance to sintering after aging play an important role.¹¹⁻¹²

Conclusions

Mesoporous zirconia materials could be prepared from sodium tris(glycozirconate) precursor using the sol-gel process without addition of stabilizers. By optimizing the sol-gel parameters in the preparation, we prepared the xerogels with high surface area (ca. $220 \text{ m}^2 \text{ g}^{-1}$ after heating at 500°C) and moderate thermal stability with heating. The use of zirconia as a catalyst or carrier is effective when the oxide has a high specific surface area that remains stable in reaction conditions. With thermal treatment, either an amorphous, or tetragonal, or monoclinic material could be simply obtained at room temperature. Zirconia was amorphous to X-ray diffraction at 400°C , with a tetragonal phase at 500°C , and a monoclinic phase at about 1000°C . Knowledge of the thermal properties of various phases would be useful for numerous technological applications of zirconia in electronic and structural materials.

Acknowledgments

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Figure Captions

- Figure 1. DTA and TGA curves of the zirconia gel obtained from the hydrolysis ratio (h) = 12
- Figure 2. XRD patterns of zirconia gels heat-treated at various calcination temperatures for (a) $h = 6$; (b) $h = 12$; (c) $h = 24$: \circ , tetragonal phase of zirconia; \bullet , monoclinic phase of zirconia
- Figure 3. Scanning electron micrographs of ZrO_2 powders obtained from $h = 12$ after calcining at (a) 500°C , (b) 800°C , and (c) 1000°C .
- Figure 4. Surface area of zirconia samples prepared at different hydrolysis ratio as a function of heat treatment temperature.
- Figure 5. Plots showing (a) Nitrogen adsorption/desorption isotherms; (b) Pore size distribution of the zirconia gel for $h = 24$ calcined at 500°C , 7 h.

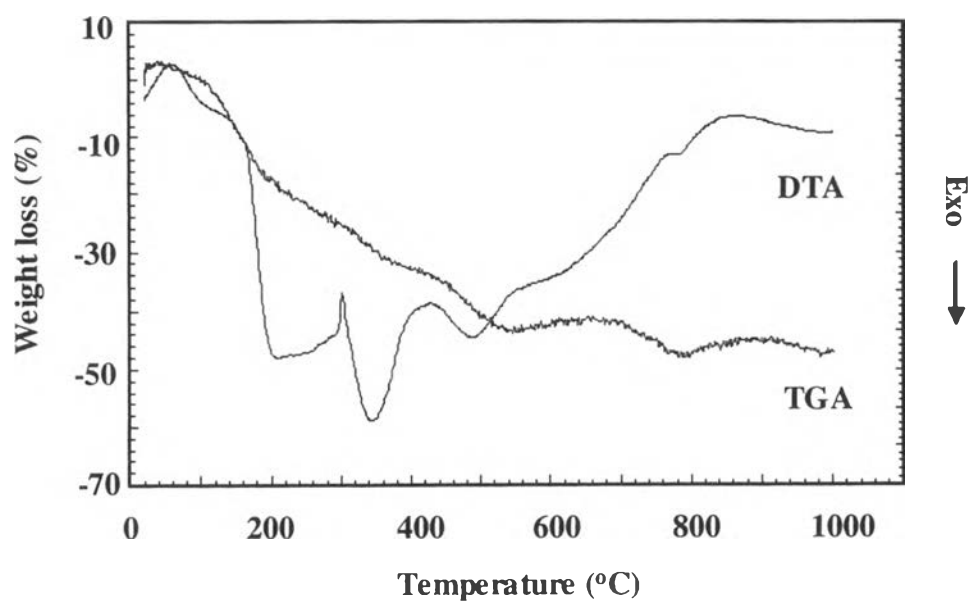


Figure 1. (Ksapabutr et al.)

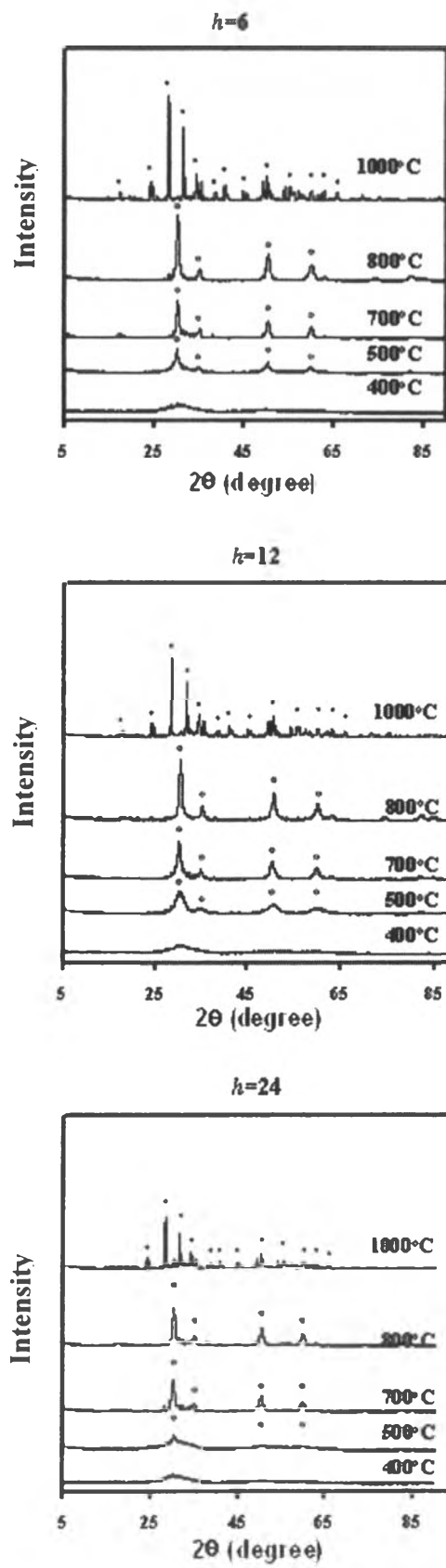


Figure 2. (Ksapabutr et al.)

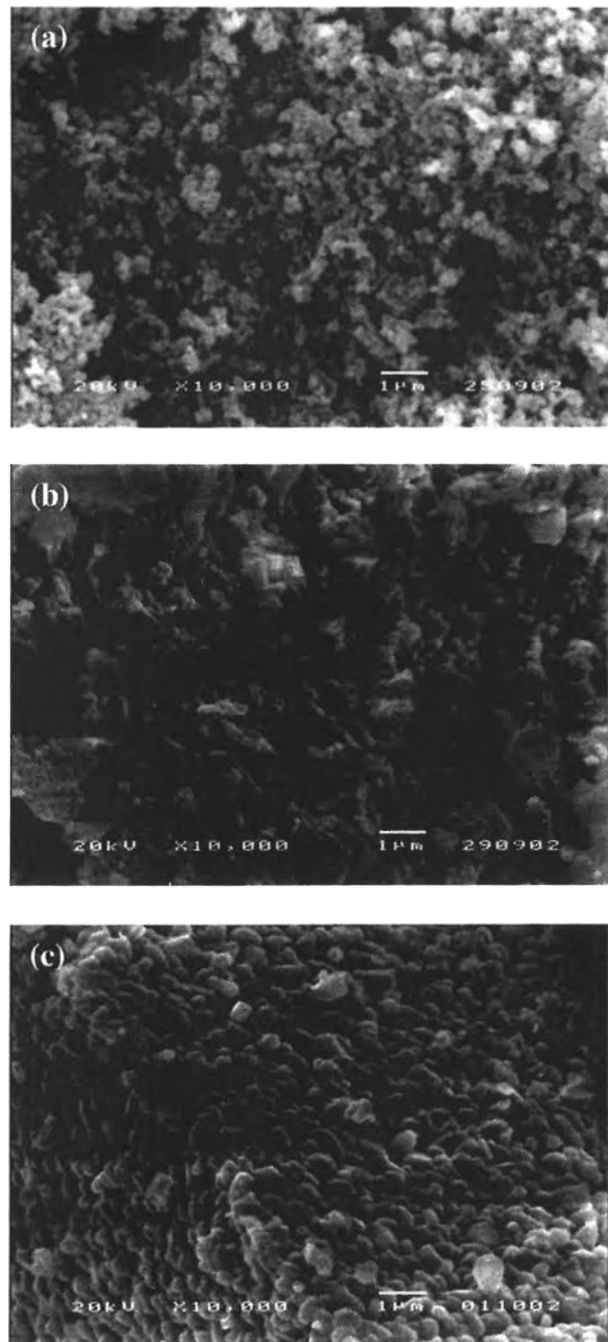


Figure 3. (Ksapabutr et al.)

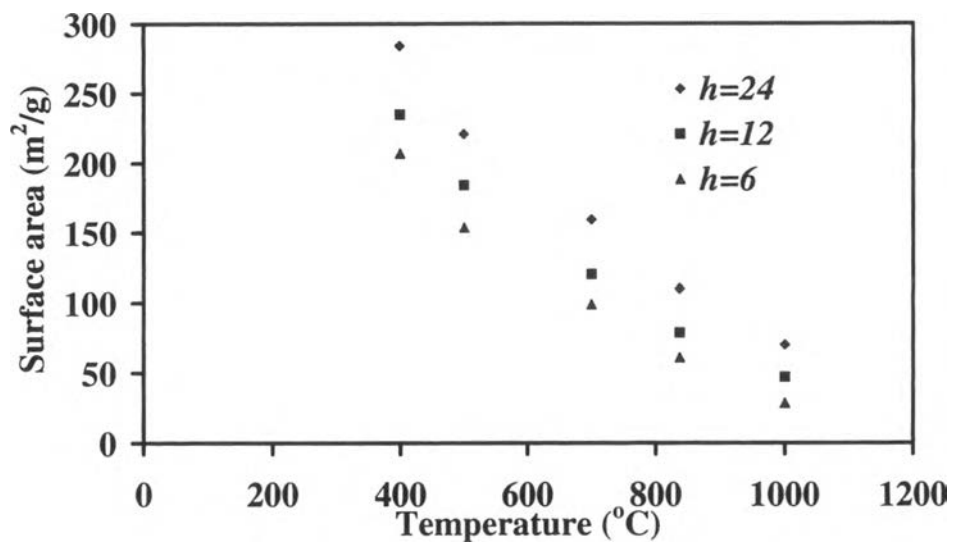


Figure 4. (Ksapabutr et al.)

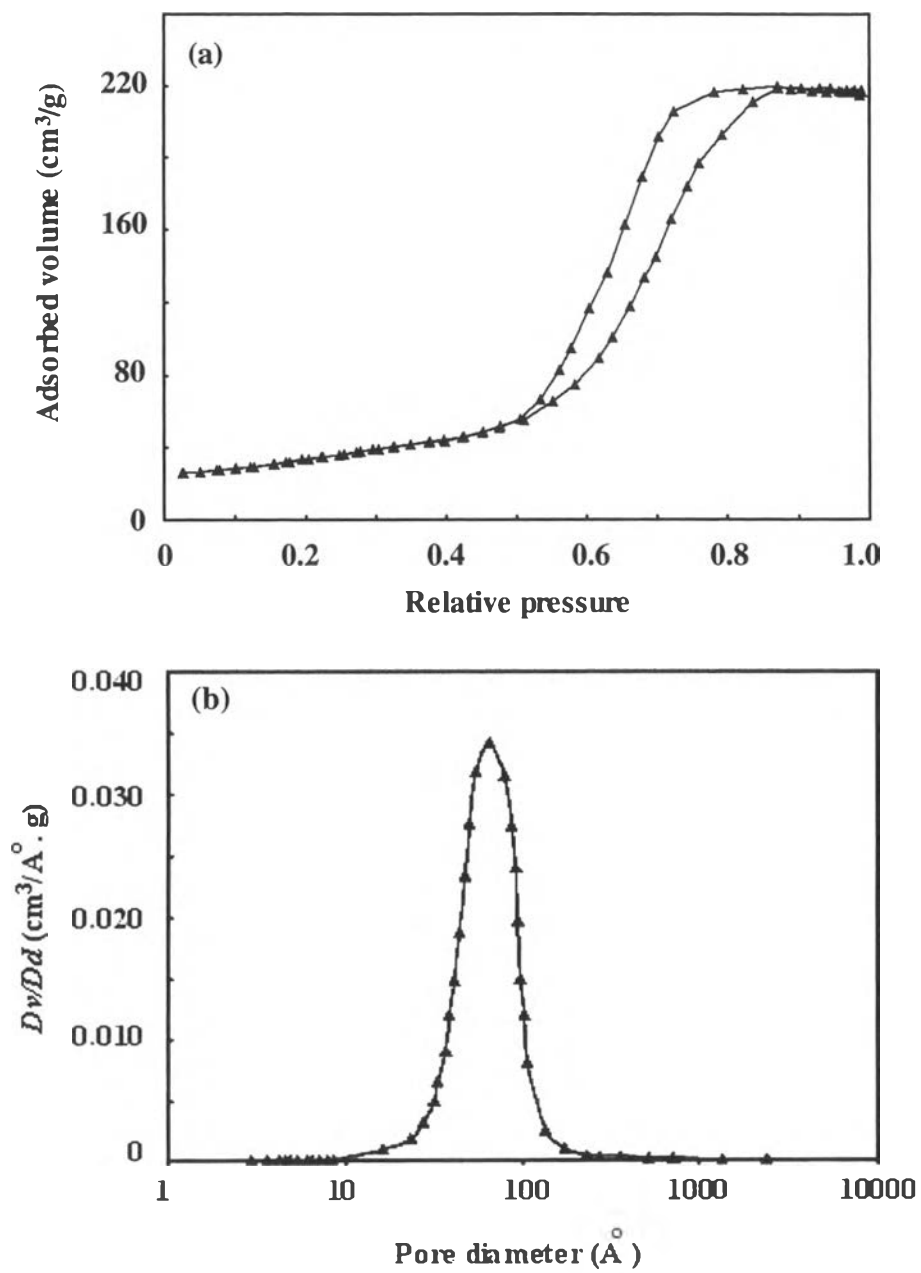


Figure 5. (Ksapabutr et al.)