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Synthesis of Nanosized Powders for Preparing Ceramic Membranes

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ABSTRACT. Magnesium-stabilized zirconia have been synthesized by a chemical route. The aim of this work is to obtain powders with suitable chemical and physical properties to be used as ceramic membranes for nanofiltration. The coprecipitation technique with an azeotropic distillation step has been employed for this purpose. Several powder characterization techniques have been utilized. The main results show that nanosized powders with high a degree of purity, high chemical homogeneity and elevated reactivity have been obtained.

INTRODUCTION

A membrane is a selective barrier between two homogeneous phases. Under a pressure gradient or sometimes under electrical potential gradient, transport of a species across the membrane can occur. Depending on the field of application, various materials have been used for preparation of membranes. Most of the membranes presently in use are made of polymeric materials. In recent years, ceramic membranes utilizing alumina, mullite, cordierite, zirconia, silicon carbide, and other ceramic materials, are receiving more attention because of their advantages over polymeric and metallic membranes. The main advantages of ceramic membranes are the elevated resistances to high temperature, abrasion and chemical attack. Moreover, ceramic membranes tolerate cleaning with caustics, acids, and any detergent, readily accommodate the abrasion found in slurries, and resist the high pressure often used in backflushing techniques [1,2].

Membranes are typically identified according to the size of the materials used in separation or to the pore size. Reverse osmosis, also called hyperfiltration, or gas separation membranes have pore sizes < 1 nm; ultrafiltration membranes have pore sizes in the range 2-100 nm; microfiltration membranes have pore sizes in the range 100-5000 nm; and membranes with pore sizes > 5000 nm are particulate filters. Inorganic membranes have been used primarily for microfiltration and ultrafiltration [1].

Applications are numerous and include food processing, beverage clarification, process gas production (nitrogen, oxygen, argon), biotechnology purifications, pharmaceutical and petrochemical industries processing, particularly for separation of macromolecules of different sizes, and other chemical and water purification processes. In addition to the separation, the membranes can also be used as catalytic agents as, for example, in hydrocarbon conversion.

The main requirements for a ceramic material to be useful as a membrane are related to the pore structure, chemical composition, and shape. The connected porosity of the membrane must be adjusted to the class of products to be separated. For this reason, ceramic membrane manufacture is concerned with macropores, mesopores, and nanopores. For gas separation dense membranes are also of interest. for this reason the major type of ceramics used in ceramic membrane manufacturing consists of refractory oxides.

Several methods are used for fabricating porous ceramics, including chemical leaching, solid state sintering, and sol-gel processing. Chemical routes are very attractive for preparing porous materials because the pore volume, size and size distribution are controllable by manipulation of chemical and physical interactions between submicron porous particles. In general, sol-gel processing can produce much finer pore sizes as well as narrower particle size distributions compared to conventional methods [3].

Recently [4], magnesium-stabilized zirconia has been suggested as a candidate for preparing a ceramic nanofiltration membrane. Nanosized zirconia powders containing 13 mol% MgO have been prepared by the sol-gel technique utilizing zirconium propoxide and magnesium ethoxide as starting materials. These commercial alkoxides are normally handled with care due to their inherent toxicity.

The aim of this work is to use a simple chemical route and comparatively low toxicity starting materials to prepare nanosized powders of magnesium fully-stabilized zirconia with suitable chemical and physical properties to be used as ceramic membranes. The coprecipitation technique with an azeotropic distillation step and chloride and nitrate salts have been used for this purpose.

EXPERIMENTAL

Zirconyl chloride (> 98%, Vetec or BDH) and magnesium nitrate (> 99%, Vetec) have been used as chemical precursors. Water solutions of these salts were thoroughly mixed in the desired proportion and added under constant stirring to an ammonium chloride solution to effect the coprecipitation. The precipitation pH was kept constant with the aid of a 1 M ammonium chloride solution. After completion of reaction, the precipitate was digestet for 2 h in the mother liquid. To remove ammonium salts the washing was conducted with a diluted ammonia solution followed by two cycles of washing with isopropanol and vacuum filtration. Complete dehydration was accomplished by azeotropic distillation with n-butanol [5,6].

A combination of thermogravimetric analysis (TGA) and differential thermal analysis (DTA) was employed to study possible thermal events resulting from removal of residual organics and gel crystallization. Simultaneous measurements of thermal effects have been carried out (Netzsch STA 409) with a heating rate of 10 °C/min up to 1000 °C and cooling rate of 15 °C/min under flowing argon. Alumina was used as reference material. The metallic impurity content in calcined samples was determined by inductively coupled plasma (ICP). The specific surface area of the powders was measured by the Brunauer-Emmett-Teller (BET) method. The BJH method was used to characterize the pore size distribution. Full nitrogen adsorption-desorption isotherms were measured using a Micromeritics (ASAP 2010) system. X-ray diffraction patterns were recorded using a Philips X'Pert MPD diffractometer with Ni-filtered Cu K_α radiation over the range of 2θ from 20° to 80°. The distribution of particles/agglomerates were measured by sedimentation using a Micromeritcs (Sedigraph model 5100).

RESULTS AND DISCUSSION

Fig. 1 shows the thermogravimetric (TG) and DTA curves of the precipitated gel after drying. The total mass loss is ~21% and is negligible for temperatures higher than 600 °C. No mass loss nor mass gain were observed during cooling. The DTA curve shows two main thermal events. The low-temperature peak is due to organic materials evolution. The high-temperature peak is assigned to the gel crystallization that occurs around 580 °C. The temperature of particle crystallization in zirconia-based solid solutions increases with the stabilizer content and occurs between 400 to 600°C.

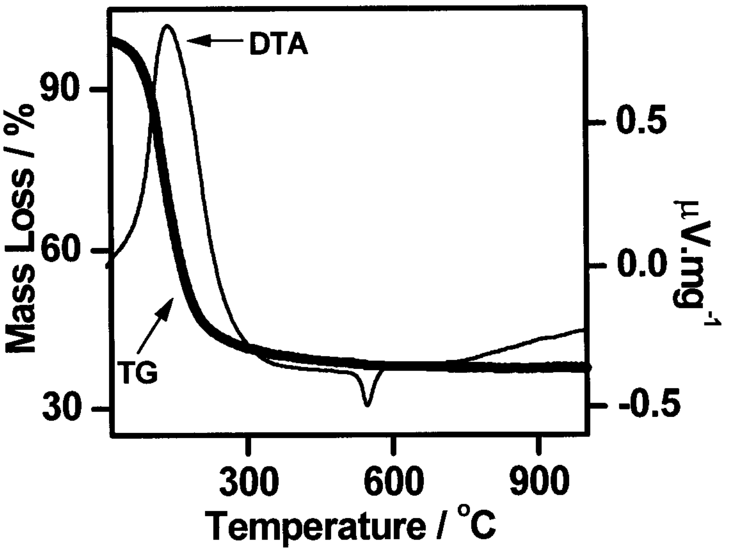

Fig. 1: TG and DTA curves of zirconia-13 mol% magnesia dried gel.

The diffraction pattern of the dried powder is shown in Fig. 2. The sample was dried in air for 48 h followed by 24 h at 100 °C.

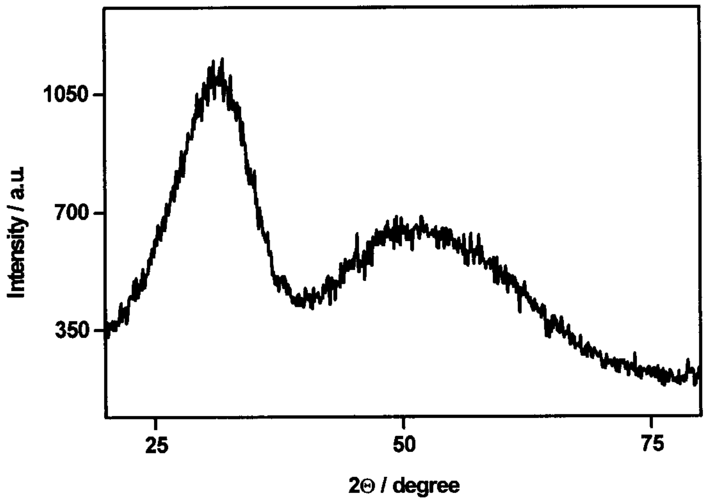

Fig. 2: X-ray diffraction pattern of the dried gel.

This pattern is typical of a sample with low crystallinity. The broad peak around $2\theta = 30°$ is characteristic of the tetragonal phase in zirconia-based ceramics.

Results of metallic impurity contents of precursor materials determined by ICP technique are in close agreement with specifications of the manufacturers. Table 1 shows the metallic impurity content after calcination.

Table 1: Metallic impurity content of the calcined powder determined by ICP.

ELEMENT	CONTENT (%)	ELEMENT	CONTENT (%)
B	0.006	Pb	< 0.0045
P	< 0.15	Sn	< 0.003
Fe	< 0.0075	Bi	< 0.0015
Cr	< 0.0045	V	< 0.003
Ni	< 0.0045	Cu	< 0.0015
Zn	< 0.15	Ba	< 0.015
Si	0.4	Co	< 0.0045
Al	0.02	Ca	0.05
Mn	< 0.0015	Sb	< 0.0045

This result shows that silicon is the major impurity though this relatively high content is normally found in commercial powders.

Fig. 3 show curves of particle size distributions determined for three powders washed with different liquids: ammonia solution and ethanol (x), ammonia solution, ethanol and isopropanol (○), and increasing the number of washing with isopropanol (△).

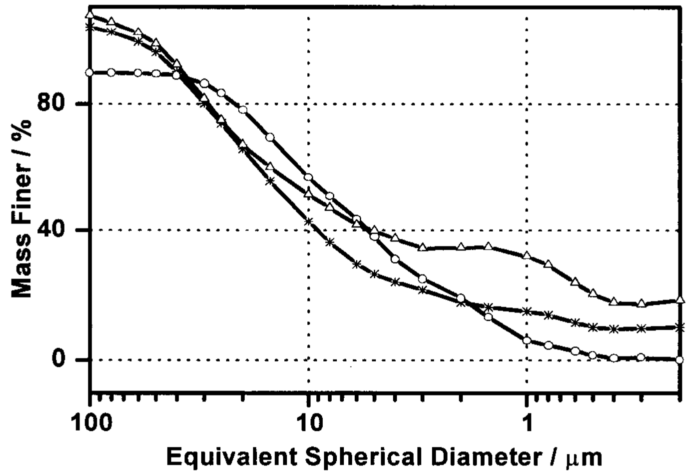

Fig. 3: Distribution curves of particles/agglomerates in calcined powders.

These curves show that the dispersion of ultra-fine particles is difficult and these results are better interpreted as distributions of agglomerated particles. In practice, a partial agglomeration of the particles may be useful to obtain high porosity final materials [3].

The specific surface (S) area of the powder after calcination at 600 °C determined by the BET method is 77 $m^2.g^{-1}$. In general, the surface area decreases with increasing the temperature of calcination. In this case, the temperature of 600 °C was used based on thermal analysis results for complete crystallization. However, it is possible to increase the time and simultaneously reduce the temperature of calcination to attain the total crystallization of the powder. The effect of increase in the time of this thermal treatment on the surface area is usually less pronounced than that of increase in temperature. From this result the equivalent spherical diameter (D) was calculated by:

$$S = \frac{6}{D.\rho}$$

where ρ is the crystallographic density. Assuming ρ = 5.9 $g.cm^{-3}$ the obtained value is 13 nm. Concerning the shape of the adsorption-desorption isotherm, it is representative of type IV (BDDT classification [7]), being characteristic of well developed mesoporous systems (pore diameter between 2.0 and 50.0 nm). The hysteresis loop is characterized by adsorption and desorption branches which are almost vertical and nearly parallel over an appreciable range of gas uptake; such loops are often obtained with agglomerates of nearly spheroidal particles of fairly uniform size and inter-particle coordination number [7].

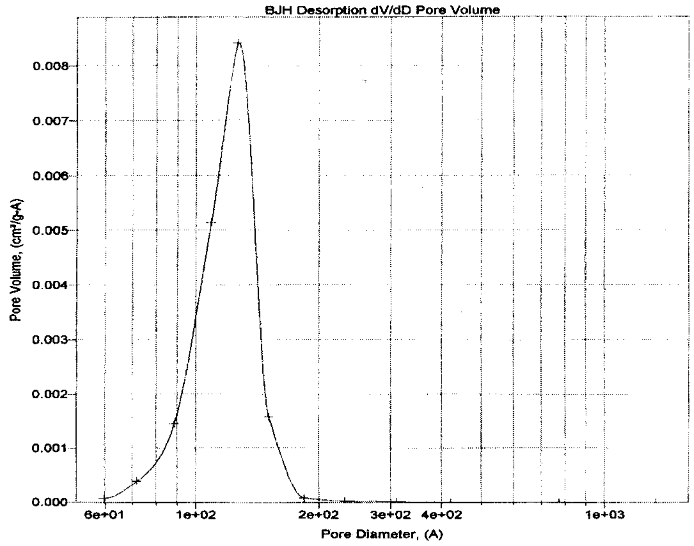

Fig. 4: Representative mesopore size distribution for powder calcined at 600 °C.

The pore size distribution as obtained by the BJH (Barret, Joyner and Halenda) method assuming a cylindrical pore model is shown in Fig. 4. The calculations were applied to the desorption branch of the isotherm. From this, the average pore diameter is 12.0 nm.

These results show that the nanosized powder prepared by the coprecipitation technique presents good chemical, physical and structural properties. The use of this powder processing technique in ceramic membrane technologies opens an alternative route to those existing.

CONCLUSION

The main conclusion of this work is that the coprecipitation technique can be used as an alternative and simple technique for preparing nanosized powders with suitable chemical, physical and structural characteristics to be used in ceramic membranes.

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REFERENCES

[1]L. M. Sheppard In Porous Materials (Ceramic Transactions **31**), ed. K. Ishizaki, L Sheppard, S. Okada, T. Hamasaki, B. Huybrechts. The Am. Ceram. Soc., Westerville, OH, 1993, p. 3.
[2] N. Das, S. Bandyopadhyay, D. Chattopadhyay, H. S. Maiti, J. Mat. Sci. 31 (1996), p. 5221.
[3]C. Guizard, A. Julbe, A. Larbot, L. Cot In Chemical Processing of Ceramics, ed. B. I. Lee, E. J. A. Pope, Marcel Dekker, New York, 1994, p. 501.
[4] R. Vacassy, C. Guizard, J. Palmeri, L. Cot, NanoStructured Mater. 10 (1998), p. 77.
[5] H. Qiu, L. Gao, C. Feng, J. Guo, D. Yan, J. Mat. Sci. 30 (1995), p. 5508.
[6] H. Shan, Z. Zhang, J. Eur. Ceram. Soc. 17 (1997), p. 713.
[7] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemieniewska, Pure Appl. Chem. 57 (1985), p. 603.

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