Synthesis of oxide ceramic powders by polymerized organic inorganic complex route

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A polymerized organic-inorganic complexation route is introduced for the synthesis of oxide ceramic powders. Polyvinyl alcohol was used as the organic carrier for precursor ceramic gel. Porous and soft powders, which have a high specific surface area, were obtained after calcinating the aerated precursors. The PVA content and its degree of polymerization had a significant influence on the homogeneity of the final powder. In particular, attrition milling process with the porous powder resulted in ultra-fine particles. In the case of the preparation of cordierite powder, nano-size powder, which has a high specific surface area of 181 m²/g, was obtained by the milling process. The complexation route was also applied to the synthesis of unstable phase in room temperature like beta-cristobalite, high temperature form of silica.

Key words: Powder, Synthesis, Polymerization, Precursor.

Introduction

Various chemical methods have been developed for the synthesis of pure, single phase mixed oxide powders with controlled powder characteristics [1-11]. In 1967, M Pechini patented a process which was used to produce niobates, titanates, zirconates, ferrites, aluminates, and silicates [1, 2, 8]. The process describes utilization of hydroxycarboxylic acids (i.e. citric and lactic acids) in combination with polyhydroxyl alcohols such as ethylene glycol to form a resin through condensation reactions. The acid acts as a chelating agent which chemically binds the cations that are dissolved in the solution. The polymerization is based on the polyesterfication between the metal-chelate complexes and polyhydroxyl alcohols. Due to the chelating action of the hydroxy carboxylic acids and the polymeric network, the cations have low mobility, so that precipitation is hindered. The result is ceramic powders with better chemical homogeneity and smaller particle size.

A rather simple-structured and inexpensive polymer, polyvinyl alcohol (PVA), can be used as the polymeric carrier [12-15]. Nitrate ions, as cation sources for oxide ceramic powders, become oxidizing agents for the decomposition of PVA. The PVA operates as a steric entrapment mechanism in the organic-inorganic solution, due to its large chain molecule. The properties of PVA depend on its degree of polymerization, degree of hydrolysis, and distribution of the hydrolyzed groups.

The hydroxyl groups hinder the solubility due to strong hydrogen bonding between the intra- and intermolecular OH group. The intra and intermolecular bonding can be reduced if there are residual acetate groups which are hydrophilic.

In this study, the polymeric steric entrapment route is introduced and the oxide powders derived from this method are reviewed.

Experimental Procedure

In the PVA process, nitrate salts were in the form of cation sources with the exception of silica which was supplied as a colloidal silica product. Diammonium hydrogen phosphate was used as the source of phosphorus. Stoichiometric amounts were dissolved in DI water and stirred for 1 h before the addition of PVA polymer (78 % hydrolyzed PVA, Airvol Series; Air Products and Chemicals, Inc., Allentown, PA, USA) solution. The 5 wt% PVA solution was made by adding 78 % hydrolyzed PVA to DI water. To examine the effect of degree of polymerization (D.P.) of PVA on the powder synthesis, two kinds of PVA was used. High-DP PVA has a DP value of 1625 (monomers/polymer), and low-DP PVA has a DP value of 428. The high DP PVA had a molecular weight of 153,000, and the low DP PVA had a molecular weight of 40,000.

The proportions of the PVA to cation sources in the solution were adjusted in such a way that there were 4, 8, or 12 times more positively charged valences from the cations than from the potentially negatively charged -(OH) functional groups of the polymers. The polymeric long chains have hydroxyl groups in solution. Hence, one PVA monomer, which has one hydroxyl (OH)

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functional group, can be used as an unit for calculation of PVA content. The exact relative amount of PVA to cations in the solution can be calculated with reference to a monomeric unit of PVA.

Water was evaporated by continuous stirring during heating on a hot plate. The resulting gel-type precursor was completely dried after several hours at 100°C. The dried organic/inorganic precursors in the all cases were then ground and were calcined or crystallized at various temperatures in an air atmosphere in a box furnace. Some powders were milled using an attritor mill to examine the effects of milling on the surface area. The powders were attritor milled at 240 rpms for several hour using zirconia milling media (ball diameter : 5 mm) and isopropyl alcohol as a solvent for milling.

The crystallization behavior of each of the calcined powders was studied as a function of temperature and holding time at elevated temperatures, using X-ray diffractometry (XRD, Dmax automated powder diffractometer, Rigaku/USA, Danvers, MA). The specific surface area of the crystallized powders and attrition milled powders were obtained by five-point BET analysis from nitrogen gas adsorption (Model ASAP 2400, Micromeritics, Norcross, GA, USA). All samples for testing were kept in a dry oven to prevent hydration of the powders. The morphologies and sizes of calcined, crystallized, and/or attrition-milled powders were examined by scanning electron microscopy (SEM, Model S530, Hitachi, Tokyo, Japan) and transmission electron microscopy (TEM, Philips EM-420, Philips Instruments, Inc., Mahwah, NJ, USA).

Results and Discussion

A schematic model of the cationic entrapment mechanism is shown in Fig. 1. The amount of polymer and its molecular length can affect the distribution of cations. The optimum amount and chain length of PVA give uniform distribution of cations and result in a pure, highly reactive, and homogenous powder at the molecular level. Whereas excess or not enough polymer results in large particle size distributions. It is speculated that weak hydrogen bonding in the hydrated PVA promotes homogeneous physical entrapment between the -(OH) hydroxyl groups and cations which are solvated by water molecules. The PVA process also produces carbonaceous material that gives heat through its combustion, so that fine and single phase powders can be formed at a relatively low external temperature. For systems in which not enough polymer is used, agglomeration may occur. Upon burnout, the agglomerated cation precursors lose much of their organics in the outer regions. Due to the intense heat evolved from the oxidative process, polymer and organic components remain within the shell. Further application of heat causes the organic to decompose into gases and expand, and makes oxides by combustion synthesis.
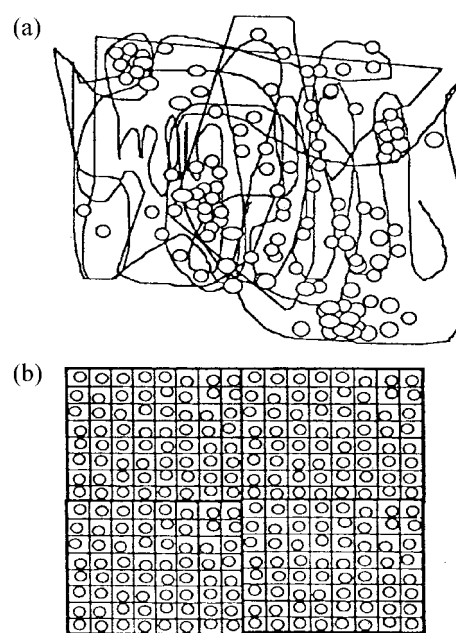
Fig. 1. Schematic model of cationic entrapment with (a) non-optimal amount of polymer and (b) optimal amount of polymer.

The less-agglomerated particles have lost most or all of the organics with application of heat. Thus, a large powder particle size distribution is observed. To maximize the powder properties, a balance is needed between the precursors and the amount of polymer [15].

The organic-inorganic precursors derived from the PVA process resembled an aerogel and were formed by the development of foam during the stirring and solution drying process. The foam was generated during evolution of NO_x gas caused by the decomposition of the nitrates. The expansion of the gel due to the evolving NO_x gas continued until the precursors dried completely.

The summary of oxide powders prepared by the inorganic-organic polymerization method are listed in Table 1. Most of cases, the calcination temperatures were below 800°C in an air atmosphere. This means the carrier polymers were easily burnt out by the oxidation process. The crystallization temperatures showed a difference for each case. In some powders, the crystallization temperatures were much lower than those of other powders prepared by other chemical synthesis. In the case of alumina, the crystalline development was different according to the D.P. (degree of polymerization) of polymer carrier. At high D.P. of PVA, gamma phase was detected at 1100°C.

The effects of the D.P. and content of the PVA on the powder synthesis are also shown in Fig. 2. In the crystallization behavior of C_3A, the volume fraction of C_3A was determined by comparing the ratio of the integrated area of the 100 % intensity peak for CaO with the 100 % intensity peak for C_3A in XRD data. In the low-DP PVA process, the volume fraction of C_3A increased with increased PVA. The best result was obtained with low-DP PVA in a 4 : 1 ratio. This implies

Table 1. Summary of Oxide Powders Prepared by Inorganic-Organic Polymerization Method (polymeric carrier : PVA)
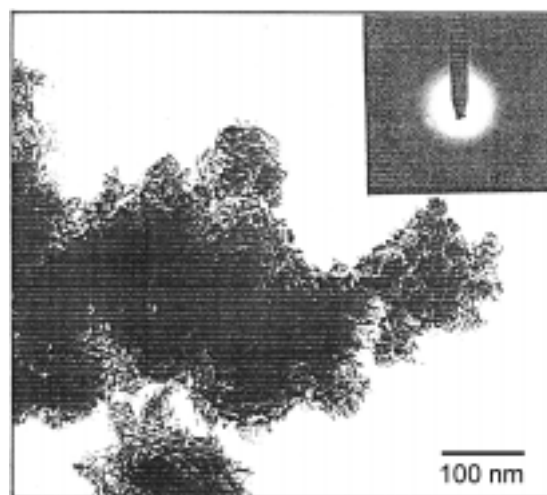
Compound	Heating temperature (°C)		Specific surface area (m²/g)		Particle size (μm)	
	Calcination	Crystallization	amorphous	crystalline	as-calcined	attrition-milled
Alumina (Al_2O_3)	800	1150	83	6.2[¥]		0.1-0.3[†]
β-Cristobalite (SiO_2)	800	1100	188			0.3
Mullite ($Al_6Si_2O_{13}$)	800	1300	157			0.1
Zircon ($ZrSiO_4$)	800	1100	81			0.2-0.3
Wollastonite ($CaSiO_3$)	800	800		18	0.7	0.2[†]
Calcium aluminate ($CaAl_2O_4$)	650	900	12		60 nm (hard aggl.)	
Belite (β-Ca_2SiO_4 or C_2S)	700	800		22.1	0.3-0.4	
Alite (Ca_3SiO_5 or C_3S)	700	1400		0.9[§]	3.0-5.0	0.2-0.4[†]
C_3A ($Ca_3Al_2O_6$)	700	1000		4.2	0.5-1.0	
C_4AF ($Ca_4Al_2Fe_2O_{10}$)	700	700		17.1	0.1-0.2	
YAG ($Y_3Al_5O_{12}$)	600	900	56	17		
Hexacelsian ($BaAl_2Si_2O_8$)	800	1100	79			0.5
Cordierite ($Mg_2Al_4Si_5O_{18}$)	800	1200	181 (attrition milled)			30 nm
Calcium phosphate (CaP_2O_6)	700	900				
Xenotime (YPO_4)	500	830	12		70 nm (hard aggl.)	

[§]after attrition milling for 1 h : 50 m²/g. [¥]after attrition milling for 1 h : 55 m²/g. [†]crystalline form
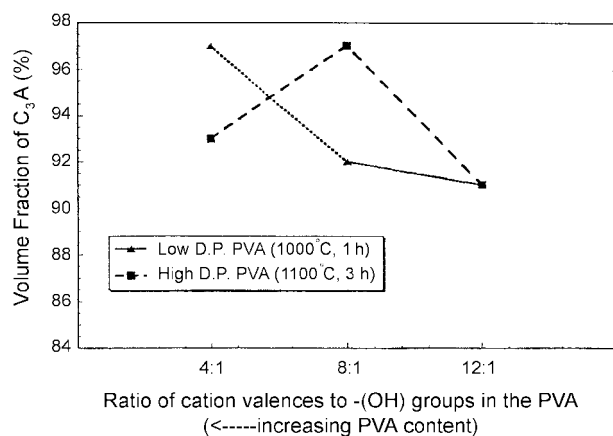
Fig. 2. Volume fraction of C_3A powder synthesized as a function of the ratio of cation valences to -(OH) groups in the PVA polymer.

Fig. 3. TEM micrograph of the amorphous-type calcined cordierite powder, which is derived from PVA solution and attrition milled for 60 min.

that, in the low-DP PVA system, the higher content of PVA did not make a significant difference in the distance between cations, but rather it improved the homogeneity of the distribution of cations. In the higher-DP PVA system, the 8 : 1 ratio showed the highest volume fraction of C_3A. This might be attributed to the high-DP PVA chain lengths being longer than the low-DP PVA ones, so that, in the 4 : 1 case, the cations could not get close enough to one another to form a compound. The solution had a high viscosity with in homogeneities caused by the entanglements of the long-chain PVA molecules in excess amount. Once this ratio was changed to 8 : 1, the results improved dramatically, because the metal ions could get close enough to one another to form C_3A. The 12 : 1 case is the most undesirable for both the low- and high-DP PVA, because there is simply not a high enough PVA content to make a homogeneous mixture.

The powders prepared by the inorganic-organic poly-merization method had extremely high specific surface areas. The polymer content and its degree of polymerization affected the surface area and morphology [14]. Some powders such as cordierite, alumina and tricalcium silicate were soft agglomerated and easily break out to fine particles after attrition milling. Despite the production of nano-size particles, the calcium aluminate and xenotime showed low specific surface areas of 12.0, and 12.0 m²/g, respectively, because the powders contained hard-agglomerated, pre-sintered particles. The TEM micrograph of attrition milled, amorphous cordierite powder are shown in Fig. 3. The powder consisted of very fine primary particles, 30 nm in size, and had a BET specific surface area of 181 m²/g (Table 1). These results were almost similar to the nano-size particles prepared by the sol-gel process [16].

Table 2. Comparison between Pechini Resin Process and PVA Polymerization Process in the Synthesis of Cordierite

Polymeric carrier	†Powder yield (%)	Residual carbon (wt%)	Particle size Distribution (μm)	Phase change
Pechini resin	27	0.07	3-50	amorphous → α
PVA solution	59	0.06	1-100	amorphous → μ → α

†Powder yield = (weight of calcined powder / weight of precursor) × 100.

The comparison between the Pechini resin process and the PVA solution process in the cordierite powder is listed in Table 2. A high yield of 59 %, which is more than double in comparison with the Pechini resin process, was observed in the PVA solution process. A small weight loss was observed during calcination in the PVA solution process. This loss was consistent with the lesser amount of PVA being used in this process, as PVA has a greater effective work of polymerization. In both cases, infinitesimal residual carbon (below 0.1 wt%) was detected in the calcined powders. The powder derived from the Pechini resin had a narrower particle size distribution of 3~50 μm than did the PVA solution process. The precursor derived from the Pechini resin could be ground easily due to the larger amount of organic carrier involved. The development of crystalline phases for each case showed different behavior. In the amorphous-type cordierite derived from the Pechini resin, the a-cordierite was formed without a sequential formation of crystalline cordierite (amorphous → μ → α). However, the cordierite derived from the PVA solution revealed the intermediate μ-phase crystalline cordierite before the crystallization of α-phase. The formation of μ-cordierite was also observed in the sol-gel powder preparation process [16]. In the synthesis of cordierite, the formation of μ-phase reduced the chances of forming other silicate compounds, such as spinel and cristobalite, or the residual cordierite-type amorphous phase [16, 17].

Conclusions

A polymerized organic-inorganic complex route was successfully employed to synthesize various monophase, fine and pure, mixed oxide powders. The new technique uses simple long-chain polymers like polyvinyl alcohol as the organic carrier for the pre-ceramic gel. The results show that metal ion chelation of the solution polymerization method is not the only mechanism to obtain molecularly homogeneous, stable precursors for complex mixed oxide powders. The cations of the mixed oxide are sterically entrapped in the entangled network of the organic polymers.

References

1. M. Pechini, U.S. Pat. No. 3 330 697, July 11, 1967.
2. M.A. Gülgün, O.O. Popoola and W.M. Kriven, J. Am. Ceram. Soc. 77[2] (1994) 531-539.
3. L.W. Tai and P.A. Lessing, J. Mater. Res. 7[2] (1992) 502-510.
4. L.W. Tai and P.A. Lessing, J. Mater. Res. 7[2] (1992) 511-519.
5. S.C. Zhang, G.L. Messing, W. Huebner and M.M. Coleman, J. Mater. Res. 5[9] (1990) 1806-1812.
6. P.A. Lessing, Am. Ceram. Soc. Bull. 68[5] (1989) 1002-1007.
7. L.W. Tai, H.U. Anderson, and P.A. Lessing, J. Am. Ceram. Soc. 75[12] (1992) 3490-3494.
8. N.G. Eror and H.U. Anderson, in Proceedings of Material Research Society Symposium (Materials Research Society, 1986) p. 571.
9. D.R. Messier and G.E. Gazza, Am. Ceram. Soc. Bull. 51[9] (1972) 692-697.
10. O.J. Sordolet, M. Akinc, M. Panchula, Y. Han, M.H. Han, J. Euro. Ceram. Soc. 14 (1994) 123-130.
11. D.M. Roy, R.R. Neurgaonkar, T.P. O'Holleran and R. Roy, Am. Ceram. Soc. Bull. 56[11] (1977) 1023-1024.
12. S.J. Lee and W.M. Kriven, J. Am. Ceram. Soc. 81[10] (1998) 2605-2612.
13. S.J. Lee and W.M. Kriven, Ceram. Eng. & Sci. Proc. 19[4] (1998) 469-476.
14. S.J. Lee, E.A. Benson, and W.M. Kriven, J. Am. Ceram. Soc. 82[8] (1999) 2049-2055.
15. M.H. Nguyen, S.J. Lee, and W.M. Kriven, J. Mater. Res. 14[8] (1999) 3417-3426.
16. H. Suzuki, K. Ota, and H. Saito, Yogyo-Kyokai-Shi. 95[2] (1987) 28-31.
17. H.Y. Jang and B.C. Lim, J. Mater. Res. 9[10] (1994) 2627-33.