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Effects of powder processing on the characterization of magnesia derived from alkoxide precursors

Part I *Preparation and characterization of powders*

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Magnesia powders have been prepared via alkoxide sol–gel and alkoxide-hydrolysis processes. Gel-derived powders exhibit porous aggregates, and extensive hard agglomerates are regarded as an intrinsic nature of gel powders; the morphology of the powders obtained from the hydrolysis–precipitate route is a function of water content and retains highly agglomerated particles, suggesting that localized microgels are formed during processing. However, a simple modified sol–gel approach proposed to synthesize fine-sized powders with a narrower size-distribution and with less hard agglomerates, has been shown to be feasible. The thermal behaviour and crystallinities of as-prepared powders are similar in all cases, however, there exists a significant difference in particle morphology. The obtained powders have been characterized and compared in the Part I of this work. Their compaction and sintering behaviour will be reported in Part II.

1. Introduction

The metal alkoxide route is versatile and can be used to prepare various products, by changing the process, such as particulate powders and/or a homogeneous gel. In the powder preparation from alkoxide precursor, there are generally two different approaches which involve colloidal chemistry in different ways [1–4], essentially by the pyrolysis or hydrolysis of alkoxides. The use of an alkoxide to obtain homogeneous glasses and ceramics via the sol–gel process has also been widely explored over the past several years [5–7]. In addition to the frequently mentioned problem of cracking, the large volume shrinkage during gelation and drying usually limits this method to shaping into small-scale products such as thin films, fibres and monoliths. The advantages and disadvantages of the alkoxide sol–gel process have been extensively discussed [8]. As well as the high purity and lower temperature of sintering, a high degree of homogeneity on the molecular scale of the product can be obtained via this method. Thus, it is reasonably expected that the gel-derived powder approach can complement the usual sol–gel process in terms of application in larger bulk specimens. It is often pointed out that gel-derived powders are very fine, reactive and chemically homogeneous [9, 10]. However, the physical homogeneity has received little attention.

We have shown previously that the sinterability of alcogel-derived magnesia powders is superior to those powders prepared via pyrolysis of the alkoxide, as the same methoxide precursors were used [11]. However, the microstructural heterogeneity was readily developed in the ground gel powder specimens. This may be largely due to a high incidence of hard agglomerates held together by solid bridges formed during gelation, essentially resulting from the polycondensation reaction that is regarded as a basic phenomenon for all sol–gel processes [5–8]. Ceramic powders are known to contain agglomerates. Generally, a hard agglomerate (also called an aggregate) is defined [12] as the primary particles that are bonded together by solid bridges (e.g. due to partially sintered or chemical reaction). In a soft agglomerate, the primary particles are held together by surface force (e.g. due to van der Waals attraction, etc.) [12], which is easily broken apart with surfactants or by mechanical force. In general, gel-derived powders are typically treated by grinding the dried or fired gels to improve the forming and sintering response. However, extensive hard agglomerates survive the subsequent milling and are indeed a major heterogeneity in ground gel powders. A similar problem can also arise in the conventional alkoxide processing based on hydrolysis of the alkoxide. The presence of hard agglomerates can have drastic effects on microstructural development during forming and sintering, thus it is important to understand and control them.

According to Dislich [5] and Yoldas [6], the formation of a polymeric gel from alkoxides generally involves two simultaneous reactions, i.e. hydrolysis and polycondensation. It is well known that the processing parameters, e.g. water content, catalyst and temperature, etc., can affect the kinetics of hydrolysis and polycondensation. The general conditions for obtaining polymeric gels have been described [5, 6] and recently reviewed [7]. However, very little attention has been paid to the alkoxide sol–gel process of magnesia. Magnesium methoxide hydrolysis with water results in fast precipitation, which is useless for further coherent polycondensation. However, it is possible to form polymeric species by controlling hydrolysis in a dilute alcoholic solution of methoxide. The hydrolytic solution can also be kept in clear sols with the addition of a certain peptizer or catalyst. Moreover, to some extent, it may be possible to control the degree of gelation by using the proper processing conditions, which in turn can also be used for improving the particle morphology of the resultant powders.

In this work, a modified sol–gel powder approach, by freeze-drying the clear sol, to avoid excessive hard agglomerates, was also proposed. Freeze-drying has been used in the powder preparation which can produce homogeneous, highly reactive powders from sulphates [13]. The purpose of the present study was to examine the effects of powder processing on the characteristics of sol–gel-derived powders that are also compared with the alkoxide-hydrolysis processing. The same alkoxide precursors were used for all the powder processes. In Part I of this study, the preparation and characterization of processed powders are described; the forming and sintering behaviour are qualitatively investigated in Part II [14].

2. Experimental procedure

Three batches of magnesia powder were prepared from magnesium methoxide [$Mg(OCH_3)_2$]; one was obtained using conventional alkoxide processing, and the others via sol–gel routes which involve first the formation of well-dispersed clear sols. Magnesium methoxide was synthesized from the reaction of magnesium turnings (RDH) and methyl alcohol (RDH), and a small amount of iodine was used as a catalyst. After filtration and vacuum drying, the as-prepared powder alkoxide was hydrolysed in excess water (100 mol water per mol alkoxide) for alkoxide processing, after which the precipitated powders were dried in an oven at 80 °C and then ground into powder. Powders obtained from this process were labelled PPT powders. A lower excess water content (with 10 molar ratio of water to alkoxide) was also used to examine the effect of water content on the particle morphology. In the sol–gel routes, hydrolysis was controlled in a dilute alcoholic solution of magnesium methoxide and peptization of the sol solution with ammonia water. The molar ratio of water: alkoxide: base was 100 : 1 : 0.1. The resultant clear sol was gelled and dried in an oven at 80 °C, and subsequently the dried gel fragments were milled into powders in an agate mortar. On the other hand, the well-dispersed clear sol was rapidly frozen by immersing into liquid nitrogen to make the sol prefrozen and coated on the inner wall surface of the flask, and then removing the water by sublimation using a commercial freeze-dryer, with care to avoid any liquid phase formed. Powders derived from this low-temperature drying route were labelled LT powders; in contrast, the ground gel powders were named HT powders. Alkoxides were used without purification, and hydrolysis was conducted at room temperature for all processes.

The rheological properties of the sol solution under various system concentrations were characterized by viscosity measurement at 40 °C in a thermostatic water bath with a Brookfield viscometer (model LVDV-II +).

Differential thermal analysis (DTA) and thermogravimetry (TG) of these as-dried powders were performed in flowing air at a heating rate of 10 °C min^{-1} to 600 °C (Seiko SSC 5000); the phase evolution of dried and calcined powders was identified by X-ray diffraction (XRD) analysis with CuK_α (Shimadzu XD-5) target. Agglomerate particle size, size distribution and state of agglomeration of the processed powders were qualitatively examined by scanning electron microscopy (SEM; JSM-T330, Jeol), transmission electron microscopy (TEM; JEM-2000cx, Jeol), light-scattering particle-size analysis (ELS-800, Otsuka), and BET surface area measurement (Micromeritics ASAP 2400). All calcined powders were obtained by firing the as-dried powders at 500 °C for 2 h in air prior to characterization.

3. Results and discussion

3.1. Thermal analysis

Fig. 1 shows the TG and DTA curves of the as-dried

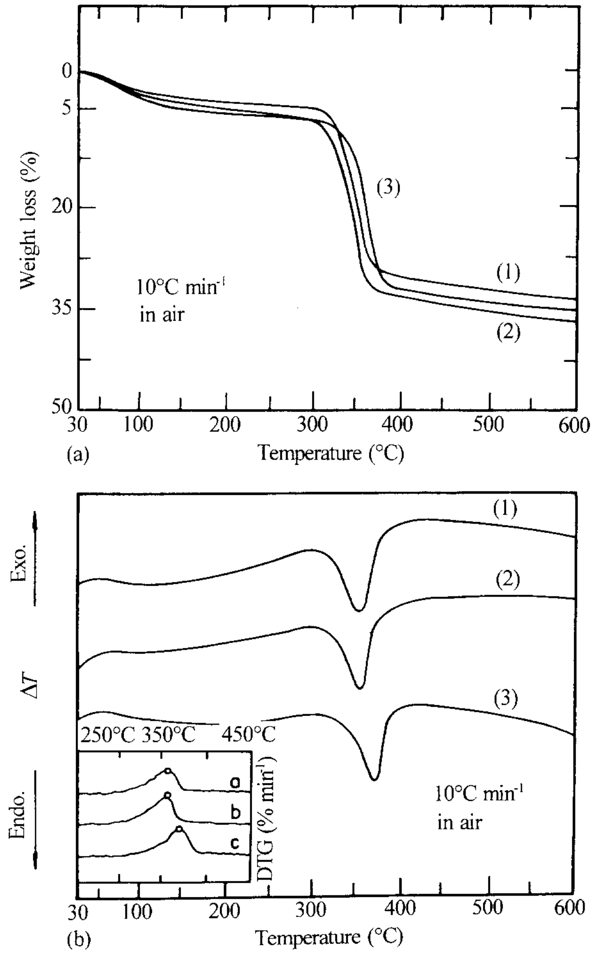

Figure 1 (a) TG and (b) DTA curves for (1) HT, (2) LT and (3) PPT as-dried powders. [water]/[methoxide] = 100.

PPT, HT and LT powders, respectively. TG curves indicate there are main weight losses between 300 and 400 °C in these powders. The PPT powders seemed to decompose at a higher temperature than the others. DTA curves show the mainly endothermic peak of PPT powders at 371.8 °C which is also higher than that at 356.5 °C for both the other powders. DTG peaks of these powders were seen around 353.9, 352.7 and 367.9 °C for HT, LT and PPT powders, respectively. The thermal analysis did not show any evident difference between the three powders, and both sol–gel-derived powders can be regarded as essentially identical in their thermal reactivity.

From the examination of X-ray diffraction patterns, the structure of the wet gel present was a weak crystalline brucite phase. This may be due to the residual alcohol and alkoxy groups that would disorder the structural determination. However, as confirmed by X-ray diffraction results, the three as-dried powders are mainly brucite phase. After drying at 150 °C for 2 h in air, they were found to be well-crystallized $Mg(OH)_2$ phase in all cases. Thus, the main weight loss in these powders was largely due to the dehydration of magnesium hydroxide and removal of some of the residual organics. X-ray diffraction patterns showed these as-dried powders all to produce magnesia by calcining at 500 °C for 2 h in air.

3.2. Characterization of the sol solution

Generally speaking, the hydrolysis of magnesium methoxide is rapid and forms cloudy precipitates. However, precipitation can be avoided by hydrolysing in the dilute alcoholic solution with ammonia peptizers and subsequently a homogeneous gelation can result. After being peptized, no precipitation was observed during this step, and resulted in a clear and low-viscosity sol. Fig. 2 shows the viscosities of as-peptized sols as a function of time under various system concentrations. The viscosity–time dependence of several sol–gel systems has been used to improve the spinability or to study the structural evolution of a gel [15, 16]. It is well established that the viscosity–time dependence is directly related to the solution structure of a sol. Viscosity measurements have also been used to define the point of gelation that is associated with the abruptly sharp increase in viscosity. As shown in Fig. 2b–d, the viscosity does not change significantly with time and is independent of shear rate in the initial period. When the solution is concentrated by evaporation, the sol solution exhibits a thixotropic rheology (i.e. viscosity depends on shear rate), and gel formation is time dependent. Thus, the viscosity of a peptized sol is dependent on the rheology of the liquid phase and on the interaction between particles in a sol. The sharp increase in viscosity near the gelation point also suggests that interparticle bonding occurs. In Fig. 2, the sol–gel transition can be catalysed by the addition of a base. Fig. 2a also shows that the viscosity for the highly basic solution with lower water content, increases drastically in the initial stage. In this case, the particles are assumed to aggregate just after peptization at the given temperature and to induce a rapid increase of viscosity from the initial stage.

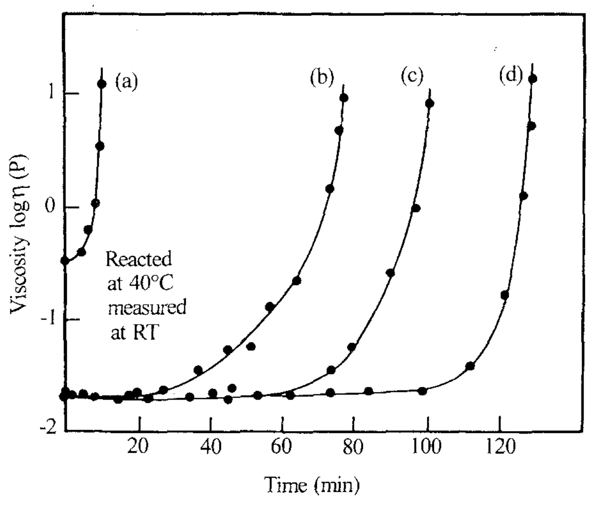

Figure 2 Variation of viscosity of the peptized sols reacted at 40 °C measured at RT under different composition conditions. Molar ratios of methoxide/water/base: (a) 1:50:0.3, (b) 1 : 100 : 0.3, (c) 1 : 100 : 0.2, (d) 1 : 100 : 0.1.

However, under proper control, the peptized clear sol can maintain a very low viscosity in the initial period that is dependent on solution concentration and predominantly by the reaction temperature under given processing conditions. During this period, the suspended particles mutually repel each other, indicating that the dispersed particles have similar surface chemical properties. Thus, it can be considered that, during the initial Newtonian period of ageing, interparticle bonding had not yet pronouncedly occurred. Furthermore, it can be thought that the hydrolysed particles are so small that the sol-flow behaviour is little influenced by particle–particle interaction. That is, the flow behaviour of a dilute clear sol is qualitatively similar to a suspension of colloidal particles with a low solid concentration. Thus, one may speculate that to prevent interparticle bonding or solid bridges forming before gelation, might be possible to reduce the extent of hard agglomeration.

When a wet gel is dried, the generally macroscopic sequence which follows involves progressive shrinkage, hardening, and fragmentation. Fig. 3 shows a typical relationship between the weight loss and drying time of a wet gel during isothermal drying at 80 °C. Drying occurs in two stages; first, the main weight loss is accompanied by volume shrinkage and fragmentation, and then loss of internal liquid at a slow rate. Essentially, the drying process of gel specimens consists in eliminating the large amount of interstitial liquid, resulting in a large volume shrinkage and further condensation. The cracking mechanisms of alkoxide-derived gel have been well discussed, and attempts have been made to overcome this well-known problem [7]. However, from the fact that the sharp increase in viscosity accompanying gelation of the sol solution is near the gelation point and the irreversible shrinkage of dried gel, both phenomena strongly suggest that the chemical bonds are substantially formed and hard agglomeration is indeed an intrinsic nature of gel-derived powders.

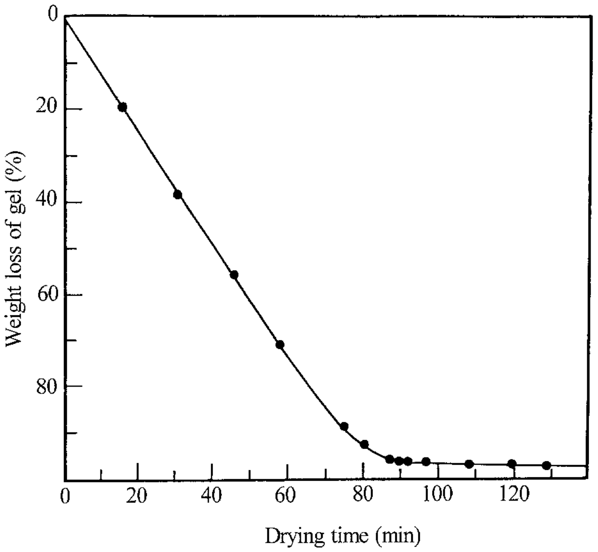

Figure 3 Typical drying curve for a wet gel dried at 80 °C in air, measured at RT. Molar ratio of water/methoxide/base = 100:1:0.1.

3.3. Powder characterization

Fig. 4 shows the particle morphology of as-dried PPT powders varied considerably as a function of water content. In the case of lower excess water (10 molar ratio to alkoxide), some of the powders exhibit a glassy appearance with a sharp-edge, as clearly observed in Fig. 4a. This morphology is very similar to the typical texture of gel-derived silica and alumina particles [18], which suggests that localized microgels are formed. On increasing the water content to 100 mol/mol alkoxide, the particles become much finer and remain highly agglomerated, as shown in Fig. 4b. Apparently, water content plays a critical role in affecting the particle morphology and the degree of agglomeration. Generally, under excess water, the hydrolysis and precipitation rate were more rapid, resulting in the formation of agglomerated precipitates. The precipitated hydroxide particulates are unsuitable for polycondensation. However, hydrolysis is difficult to complete even under a large excess of water, and residual alkoxy groups should cause localized condensation during hydrolysis and subsequent drying. The extent of this localized condensation is determined by the water content at a given reaction temperature. Presumably, the mechanism of interparticle bonding leading to microgels or aggregated precipitates involves the attachment of two neighbouring hydrolysed particles via the formation of oxygen bridges by condensation. Thus, to obtain a homogeneous gel depends mainly upon proper control of the relative rate of hydrolysis and condensation, and a partial hydrolysis of methoxide is implemented to introduce the polymeric species which can be used to form a network structure. This can be easily facilitated using water content, dilution, catalyst and reaction temperature as critical processing variables, as shown in Fig. 2.

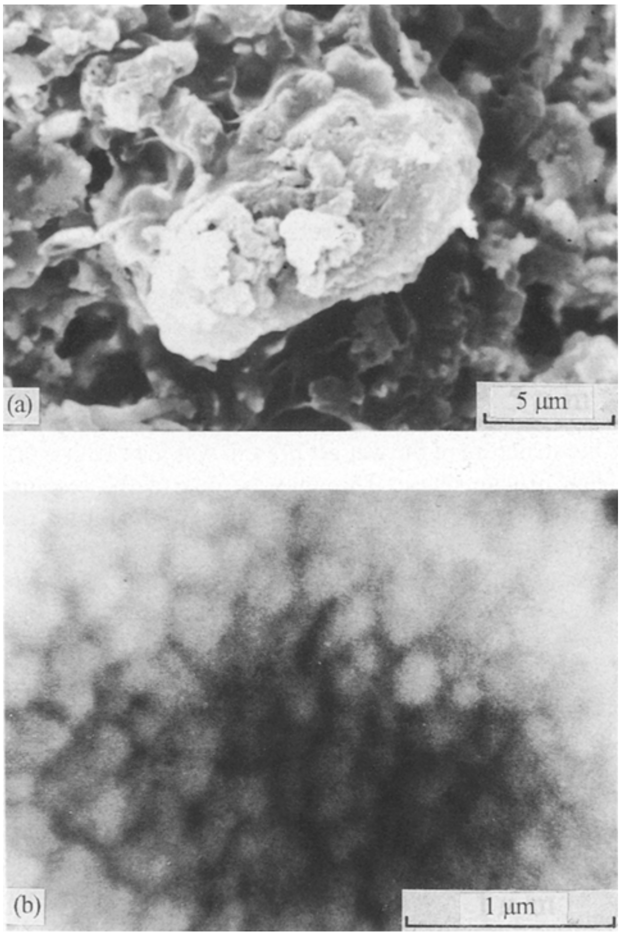

Figure 4 Scanning electron micrographs of PPT as-dried powders produced via hydrolysis of methoxide with (a) 10 mol, and (b) 100 mol water.

In the sol–gel route, hydrolysis is carried out in a dilute alcoholic solution of methoxide and the precipitated particles also immediately agglomerate in solution. The peptization step following this allows break-up of the agglomerates and results in an aqueous, transparent, low-vicosity sol. This sol consists of fine-sized particles very evenly distributed throughout the solution. Gelation can be brought about either by concentrating the sol solution under evaporation, or by ageing. Fig. 5 shows the scanning electron micrographs of 0.1 mol base catalysed sol–gel-derived powders. It is clearly seen that HT powders exhibit angular particles with irregular sharp edges and with extensive hard agglomerates. In contrast, LT powders are predominantly soft agglomerates, which appear to be looser and finer, as well as having an agglomerate particle-size distribution which was narrower than HT powders. The details of the substructures of aggregated HT powders was also examined on a higher-magnification scanning electron micrograph as shown in Fig. 6. It can be seen that the constituent particles are interconnected and linked together into a network structure that also reveals the hard agglomerated particles to be porous. It is apparent that gel-derived powder is essentially an agglomerate of elementary particles which crosslink to form extensive hard agglomerates that also survive the subsequent milling. Thus it can be thought that the constituent particles are coated with residual alkoxy and hydroxy groups which are eliminated during condensation, leading to substantial formation of interparticle bonding. However, in the case of LT powders, the size and degree of

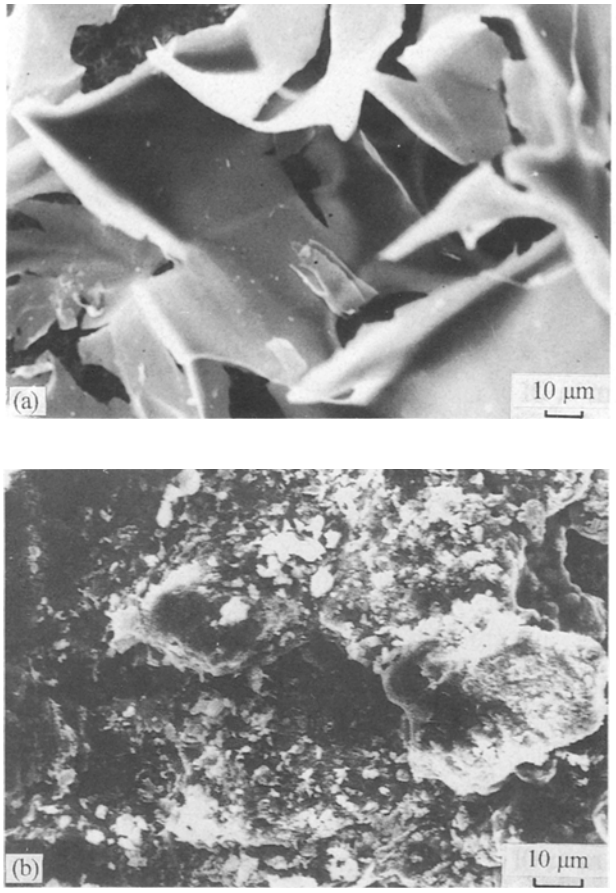

Figure 5 Comparison of scanning electron micrographs of sol–gel-derived (a) HT and (b) LT as-dried powders.

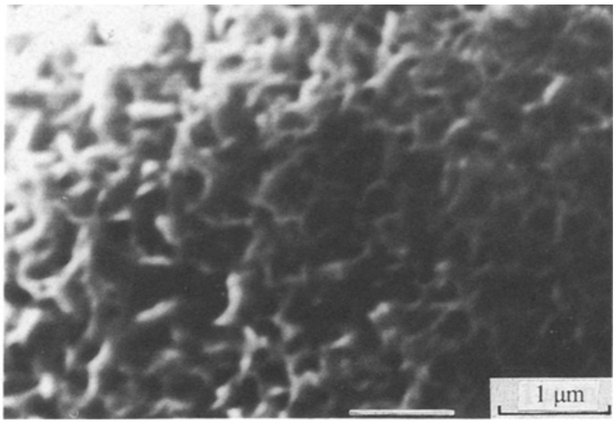

Figure 6 Higher magnification scanning electron micrographs of a hard agglomerate HT powders, showing details of the substructure of the aggregates.

hard agglomeration can be efficiently reduced by this powder approach. This suggests that a processing change, to prevent strong interparticle bonding taking place before gelation, is feasible. After drying, loose and fine LT powders with some very friable agglomerates can be obtained which are readily broken up by slight vibration without additional milling.

The comparative TEM observation of these differently processed powders is shown in Fig. 7. In the case of PPT powders and ground gel powders (HT powders), as shown in Fig. 7a–d, the irregular state of the agglomerates with highly aggregated particles was also clearly observed, in both the as-dried or calcined powders. It is considered that localized microgels were formed within PPT powders, thus some similarity in aggregate morphology between both powders is not surprising. For PPT powders, most of the soft agglomerates were formed in the precipitates by the coagulation of hydrate products, while a certain amount of hard agglomerates usually formed during drying. This implies that a partial condensation would occur in local regions during processing, and the growth of aggregates would be more pronounced after drying and calcination. Fig. 7c and d show that the results of as-dried HT powders are similar to those observed by SEM, in which the extensive hard agglomerates also survive the calcining. It seems that an extensive hard agglomeration is a general characteristic of gel-derived powders. Sacks and Pask [19] demonstrated that the gelled mullite powders agglomerated on drying and hard agglomerates formed during calcination. In contrast, Fig. 7e and f show that as-dried LT powders consist of fine-sized particles that have a more uniform shape with narrower size distribution after calcining, although some of them seem to be superimposed on each other.

The results of the evaluation of specific surface area and light scattering of these as-dried and calcined powders are summarized in Table I. After calcining at 500 °C in air, the LT magnesia powders have a finer agglomerate size and narrower size distribution with a mean particle size of 48 $\pm$ 5 nm, which is consistent with the evaluation by BET surface area (36.5 $\mathrm{m^2\,g^{-1}}$) equivalent particle diameter, where free spheres were assumed. For HT magnesia powders, the mean particle size and BET surface area are 610 $\pm$ 255 nm and 49.2 $\mathrm{m^2\,g^{-1}}$, respectively, indicating that this highly aggregated particle is also porous, as in the as-dried powders. According to light-scattering analysis, the HT as-dried and calcined powders all have a higher percentage of coarser aggregated particles than the relative LT powders, which results in a larger mean particle size and a higher standard deviation. PPT powders also reveal porous aggregates, the growth of which is more pronounced after calcination. These results are consistent with the microstructural observations.

It is worth noting that HT and LT as-prepared powders are considered to be essentially identical in their thermal behaviour and crystallinities, as characterized by the results of thermal analysis and X-ray diffraction, but their physical properties show a great difference. Although it can be thought that the ground gel powders have a high reactivity due to their high surface area, the presence of extensive hard agglomerates must be avoided in order to achieve a homogeneous microstructure. However, the ground gel powder route inherently lacks an approach for controlling the hard agglomeration, because the strong solid bridges are ubiquitous. However, enhanced aggregate size reduction without milling can be observed with the LT powder approach in which large agglomerates or clusters formed during hydrolysis/polycondensation were removed by peptization. During the initial

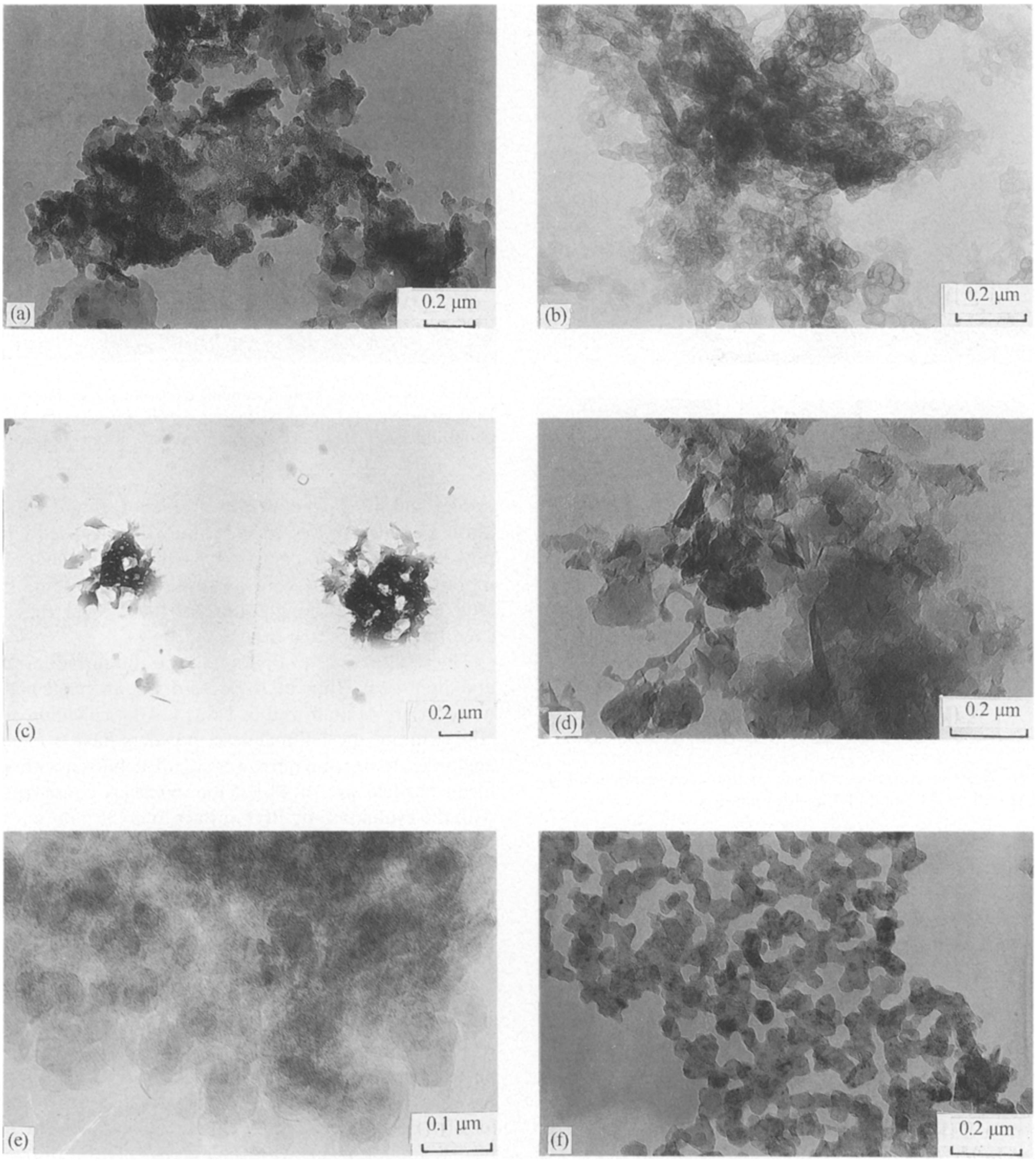

Figure 7 Comparison of transmission electron micrographs of as-dried (a) PPT, (c) HT, and (e) LT powders, and as-calcined (b) PPT, (d) HT, and (f) LT powders.

Newtonian period, a quick-freezing treatment could also provide a possible approach to prevent the growth of polymeric species or particle clusters, and to retain the possibly initially well-suspended state. Thus, after freeze-drying, resultant fine powders with narrower size distribution and with fewer hard agglomerates are frequently feasible.

4. Conclusions

It has been demonstrated that fine-sized and high surface area MgO powders can be synthesized from alkoxide precusors and the particle morphology varied with different processing conditions. The extensive hard agglomerated particles within ground gel powders are unavoidable as a consequence of the gelation effect. Powders obtained from the hydrolysis of methoxide contained a certain amount of porous aggregates. However, a processing change via a sol approach, followed by freeze-drying, can provide a practical means of reducing the degree of hard agglomeration, and also of providing better control and reproducibility of physical properties of the prepared powders than by the other routes.

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TABLE I Specific surface area, S_v, and equivalent particle size, d_S, as well as light scattering mean particle size, d_L[a], of processed powders

Powders	S_v(± 10%m^2g^{-1})		d_s(nm)		d_L(nm)	
	(1)[b]	(2)[b]	(1)	(2)	(1)	(2)
PPT	61.8	42.0	41.0	40.0	85 ± 22	225 ± 83
HT	93.4	49.2	27.0	34.0	513 ± 251	610 ± 255
LT	64.4	36.5	39.0	46.0	43.6 ± 12	48 ± 5

[a] Number basis.

[b] (1) As-dried state, (2) powders obtained from calcining at 500 °C for 2 h in air.

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