

Porous mullite and mullite-based composites by chemical processing of kaolinite and aluminium metal wastes

José Pascual,^a José Zapatero,^a María C. Jiménez de Haro,^b Ignacio Varona,^b Angel Justo,^b José L. Pérez-Rodríguez^b and Pedro J. Sánchez-Soto^{*b}

^aDepartamento de Ingeniería Civil, de Materiales y Fabricación, Escuela Técnica Superior de Ingenieros Industriales, Campus del Egido s/n, Universidad de Málaga, 29013-Málaga, Spain. E-mail: jpascualc@uma.es

^bInstituto de Ciencia de Materiales, Centro Mixto Consejo Superior de Investigaciones Científicas (C.S.I.C.)-Universidad de Sevilla, c/Américo Vespucio s/n, Isla de la Cartuja, 41092-Sevilla, Spain. E-mail: pedroji@cica.es

Received 8th June 1999, Revised manuscript received 29th November 1999, Accepted 15th March 2000
Published on the Web 11th May 2000

Porous mullite and mullite-based composites have been prepared from a chemical processing route starting from a precursor obtained using an aqueous suspension of kaolinite and aluminium hydroxide. This was coprecipitated with kaolinite using ammonium hydroxide or hexamethylenediamine (HMDA), and a solution of aluminium chloride prepared from dissolved recycled wastes of aluminium metallic powders. Raw and ball-milled kaolinite during 30 minutes have been employed. The precursors and the obtained materials were characterized by X-ray diffraction (XRD) and thermal diffractometry, simultaneous differential thermal analysis (DTA) and thermal gravimetric analysis (TGA), scanning electron microscopy (SEM), flexural strength test at room temperature and Hg intrusion porosimetry. The feasibility of using HMDA as a precipitating agent in the proposed chemical processing route for mullite preparation has been demonstrated. The advantageous use of HMDA, as compared with ammonium hydroxide, and ground kaolinite, as compared with raw kaolinite, produced single-phase mullite materials and enhanced the flexural strength of the resultant ceramic porous bodies by firing at 1550–1600 °C (porosity 50–45 vol%). These materials would have application as refractories, substrates, filters and thermal isolating materials.

Mullite (nominal composition $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is the only stable crystalline phase, at normal pressure, in the $\text{SiO}_2\text{-Al}_2\text{O}_3$ system. It is produced after the thermal decomposition of aluminosilicates, such as kaolinite or pyrophyllite, and clay-based materials^{1–5} and obtained by reaction sintering mixtures of kaolinite and alumina.^{6–11} Mullite is one of the most commonly found phases in industrial ceramics. However, according to Aksay *et al.*⁷ the importance of mullite as a ceramic phase in materials was only recognized during this century when the first binary phase diagram was proposed.¹² Its excellent properties, such as high-temperature strength, creep resistance, low thermal expansion coefficient, good dielectric properties, very high transmittance in the mid-IR range, good chemical and thermal stability, with retention of mechanical properties to elevated temperature and stability in oxidative atmospheres, make this ceramic and its composites important candidates for electronic, optical and high-temperature structural applications as advanced materials.^{5–7} Due to the low relative permittivity of mullite and its thermal expansion, which is close to that of silicon, this material is also being considered as a potential candidate for substituting the alumina substrates in the new generation of fast computers.^{6,7,10,11}

The preparation of pure mullite powders has been extensively reviewed in the literature.^{5,8,13} Thus, different combinations of precursors for silicon and aluminium have been used for mullite preparation, including aluminium and silicon sols from inorganic salts or alkoxides in aqueous and non-aqueous media, but the experimental conditions have to be carefully controlled.^{5,8,13} Single and diphasic gels have been prepared to fabricate mullite ceramics.

On the other hand, the reaction series of kaolinite or metakaolinite yields mullite,^{1–5} being similar to that of silica–

alumina diphasic precursors (with a scale of homogeneity from 1 to 100 nm). Initially, a transient alumina or alumina-type spinel forms at 980 °C with an exothermic thermal effect, and mullite crystallization follows at higher temperatures, often with a distinct second weak exotherm at *ca.* 1200 °C, which could be also due to the formation of a metastable eutectic liquid.^{9,10} Kaolinite is an atomically layered structure of $(\text{Si}_2\text{O}_5)^{2-}$ and $[\text{Al}_2(\text{OH})_4]^{2+}$ molecular sheets, but the level of mixing of Si and Al is not sufficient to prevent the segregation of alumina and amorphous silica, which crystallizes as α -cristobalite at high temperatures.^{4,5} However, mullitization can be produced at high temperatures by reaction sintering mixtures of kaolinite and alumina with an overall composition $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (72 wt% alumina and 28 wt% silica).^{10,11} In recent papers, mullite-alumina functionally gradient ceramics¹⁰ and mullite-aluminosilicate glassy matrix substrates, obtained by reactive coating,¹¹ have been prepared by this processing route. Another processing route involves the milling of aluminium or Al/Si alloys and alumina powders with additives, and subsequent oxidation to give reaction-bonded binary metal oxide ceramics.¹⁴ There are even processing routes *via* the so-called “transient viscous sintering” process, due to Sacks *et al.*¹⁵ More recently, a new processing route has been proposed, named the “oxide one-pot synthesis”, for mullite and other ceramics.¹⁶

The present investigation deals with the preparation of mullite and mullite-based composites based on a chemical processing route. Porous mullite and mullite-based composites have been prepared starting from a precursor prepared using kaolinite and aluminium hydroxide. The amorphous aluminium hydroxide has been coprecipitated with kaolinite using ammonium hydroxide (ammonia) or hexamethylenediamine (HMDA), a low-cost chemical used in the manufacture of

synthetic textile fibres, and a solution of aluminium as its chloride salt, resulting from dissolution in HCl of aluminium metal shavings coming from the recycled wastes of aluminium metal manufacturing. This processing route may be considered a cheap and promising process for recovery of aluminium metal wastes as an alternative process to recycling by remelting, thus avoiding the problem of other by-products. The precursors and the obtained mullite materials have been characterized mainly by X-ray diffraction (XRD), thermal methods, Hg intrusion porosimetry and scanning electron microscopy (SEM).

Experimental

Preparation of mullite-based precursors

A raw kaolinite from Caobar (Poveda, Guadalajara, Spain) with kaolinite content >90 wt%, and quartz (*ca.* 10 wt%) and some mica, was used. The chemical composition (in wt%) is: SiO₂ 47.98, Al₂O₃ 38.10, Fe₂O₃ 0.57, TiO₂ 0.16, CaO 0.07, MgO 0.20, Na₂O 0.04, K₂O 0.43 and a weight loss after heating at 1000 °C amounting to 12.26 wt%. Raw (Kaolinite sample A, particle size <2 µm 45.4 wt% determined by sedimentation) and ball-milled kaolinite for 30 minutes (Kaolinite sample B, particle size <2 µm 96.4 wt%) were used. Fig. 1 shows the X-ray powder diffraction (XRD) patterns corresponding to these samples, where some structural disorder is produced after grinding for 30 min the original kaolinite sample. The BET surface area (measured by nitrogen adsorption) increases from 6.8 to 8.6 m² g⁻¹ after grinding.

Fig. 2 shows the processing flow-chart used for the preparation of mullite-based precursors starting from kaolinite and aluminium alloys.

Several aluminium alloys used in the manufacture of aeronautics were selected as raw materials to perform this research. In the present study, waste shavings of a particular aluminium alloy, with chemical composition (in wt%) Al 92.25, Cu 4.50, Mg 1.50, Fe 0.50, Si 0.50, Mn 0.50 and Zn 0.25, were dissolved using an aqueous solution of HCl (35 vol%). After reaction, the resultant solution was filtered, the aluminium in solution was determined by atomic absorption, and the solution was thoroughly mixed with the kaolinite aqueous suspensions prepared with samples corresponding to samples A and B in proportions such that the resulting ceramic materials after firing would be the stoichiometric mullite (72 wt% alumina and 28 wt% silica). The hydroxide was precipitated from the aluminium salt in solution using concentrated

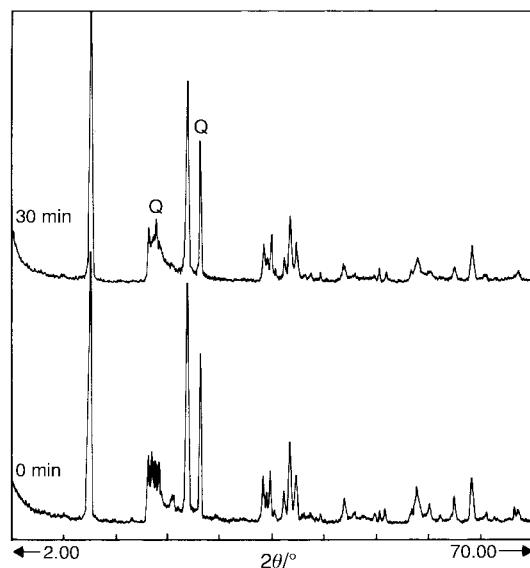


Fig. 1 XRD of original kaolinite (0 min), sample A, and after grinding for 30 minutes (30 min), sample B. Q = Quartz.

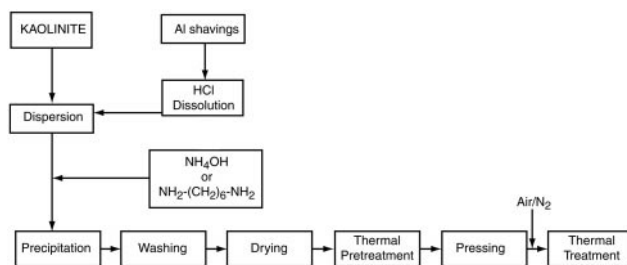


Fig. 2 Processing flow-chart.

ammonia (ammonium hydroxide) solution or hexamethylenediamine (HMDA, a low-cost chemical used in the manufacture of synthetic textile fibres) under adequate precipitation conditions. Control of the pH of the slurry (6.5–7.2, as the precipitation pH of the hydroxides is less than 8), and consequently of the metal impurities in solution, was necessary in order to avoid the presence of impurities and to achieve complete precipitation under these conditions. Cu and Zn were complexed and remained in solution, being interesting from the point of view of Al recovery and purification of the raw solution. This was checked using chemical analytical methods (atomic absorption).

After vigorous stirring and sedimentation, the coprecipitated solid (kaolinite with aluminium hydroxide obtained by reaction) was washed to eliminate the impurities and alkaline mother liquors. With subsequent drying, a portion of the solid cake was examined by XRD, showing only kaolinite and quartz as crystalline phases. The product obtained using HMDA as precipitant was thermally pretreated at 300 °C over 90 minutes under nitrogen flow to eliminate this diamine, which was not completely eliminated by simple washing as compared to when ammonia solution is employed in the precipitation.

Characterisation

Samples were studied using dynamic thermal conditions (DTA-TGA) with a heating rate of 10 °C min⁻¹ using a Setaram apparatus, model 92-16,18. These studies were performed in air with calcined alumina as reference material and Pt–Rh crucibles. Thermal treatments of cold-pressed powdered samples at 500 MPa were performed in air using a furnace at a heating rate of 10 °C min⁻¹ over 30 minutes to a maximum of 1600 °C.

X-Ray powder diffraction (XRD) patterns were obtained using oriented aggregates of ground powders on a Siemens XRD D-5000 diffractometer, using Cu-Kα radiation with a scan rate of 1 deg min⁻¹ and were compared to the JCPDS files. A temperature controlled device was also used to study some samples by thermal diffractometry from room temperature up to 1000 °C. ²⁷Al Solid-state nuclear magnetic resonance (NMR) spectroscopy using magic angle (54° 44') spinning (MAS) was performed using a high-resolution Bruker DRX400 spectrometer and an external reference of AlCl₃·6H₂O in 1 M solution at 104.24 MHz and a spinning rate of 12 KHz. Scanning electron microscopy (SEM) pictures were taken on a JEOL JSM-5400 scanning electron microscope equipped with an energy dispersive X-rays analysis (EDX) Link system for qualitative chemical analysis. Fractured samples were deposited on copper supports and covered by a thin film of gold. TEM was also used to study some samples, in particular to differentiate mullite from other crystalline phases using selected area electron diffraction patterns.

Mechanical properties and porosities of selected fired samples were studied. The flexural strength measurements at room-temperature were performed by four point bending test using an Instron machine, model 8501. The porosity was

measured by mercury intrusion porosimetry at a maximum of 400 MPa using a Fisons apparatus.

Results and discussion

The precipitated solid of raw kaolinite and aluminium hydroxide, produced by the reaction between the aluminium salt and the base (ammonium hydroxide or HMDA), was examined by XRD after washing and drying. Results showed only kaolinite and quartz as having crystalline structure, and an amorphous phase. The last likely contains aluminium oxyhydroxides produced in the precipitation stage (Fig. 2) using HMDA or ammonia. Results from an on-going study are helping to elucidate the reaction of HMDA and its interaction with kaolinite layers and aluminium oxyhydroxide coming from the aqueous solution of the aluminium salt. It is a key aspect of this processing chemical route for the preparation of mullite powders.

For a more detailed study and to investigate further the nature of this solid product, ^{27}Al MAS-NMR spectroscopy was used. This technique showed that the NMR spectrum had only a signal at 8.5 ppm. This is associated with the octahedral aluminium coordination present in the resultant product which contains kaolinite and the amorphous phase formed in the presence of HMDA. The aluminium ions are incorporated into the coprecipitated solid in octahedral sites. In this sense, it is interesting to note that Jaymes *et al.*¹⁷ suggested that hydroxylated aluminium atoms link to a mullite gel precursor, which is obtained from aluminium nitrate and tetraethyl orthosilicate (TEOS) *via* aqueous homogeneous precipitation using urea. Hydrolysis produces aluminium atoms which remain *preferentially* in an octahedral coordination (0 ppm), since the relative amount of six-fold coordinated atoms increases. Sanz *et al.*⁴ studied a sample of kaolinite of the same origin as used in this research, and found a signal of -2 ppm in their original kaolinite sample. The difference of signal and the broadening of the peak may be attributed to the existence of an amorphous phase containing Al (aluminium oxyhydroxide) and HMDA possibly bonded to a kaolinite layer, with all aluminium present in octahedral coordination.

Thermal treatments of the precipitates in air using dynamic heating conditions (DTA-TGA) are shown in Fig. 3. The first derivative of the TGA curve is also included (DTG) to show the thermal evolution. The TGA results of the mullite precursor obtained using ammonia indicate a continuous weight loss from low temperatures, which is attributed to dehydration and dehydroxylation of amorphous aluminium hydroxide. From 400 to *ca.* 600 °C, the kaolinite is dehydroxylated with the formation of metakaolinite, an amorphous phase to X-rays.^{1,4} When the corresponding mullite precursor obtained using HMDA is examined by DTA-TGA, thermal events are shown to overlap with HMDA oxidation in air, *i.e.* loss of organic species, with gas evolution. In connection with these features, several DTA effects associated with dehydroxylation (endotherm) and thermal oxidation (exotherm) of HMDA are observed. In the same way, the first derivative curve of TGA (DTG diagram) is illustrative of the thermal evolution, with maximum decomposition rates close to the DTA thermal events.

Characteristic of metakaolinite is the sharp exothermic DTA peak, with no weight loss observed at 995 °C (using ammonia) and 994 °C (using HMDA) in the samples.¹⁻⁵ The cause of this exothermic DTA peak has been controversial in the literature.¹⁻⁵ It has been attributed to the formation of either mullite nuclei or spinel ($\gamma\text{-Al}_2\text{O}_3$ solid solution) or both, since at DTA heating rates, both mullite and spinel have the possibility of forming concurrently.⁵ In the present case, after dynamic heating below 1100 °C, X-ray reflections of aluminium oxide (according to JCPDS No. 29-0063), as a nanocrystalline

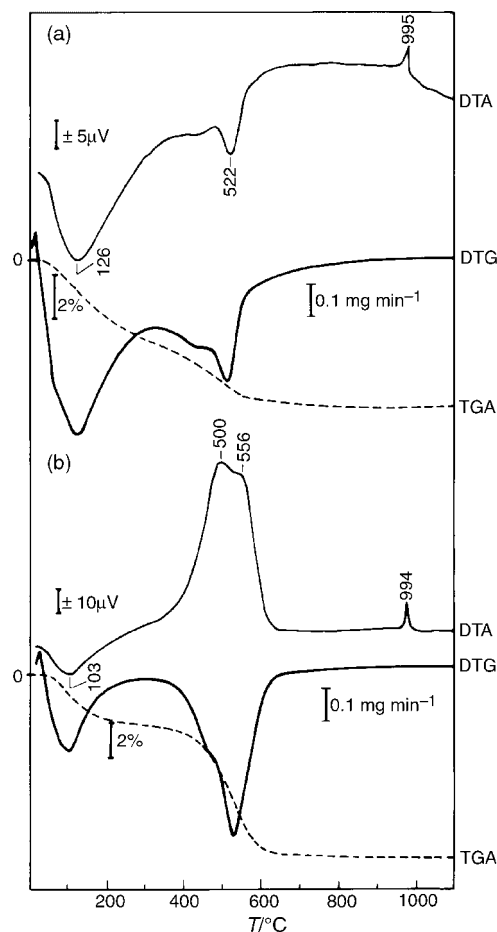


Fig. 3 Thermal analysis by DTA and TGA of the mullite precursor samples prepared using (a) HMDA and (b) ammonium hydroxide as base precipitating agents. Heating rate: $10^\circ\text{C min}^{-1}$. The first derivative of the TGA or DTG diagram is also included.

material, quartz, and an amorphous phase were observed. Impurities present in kaolinite influence the size and temperature of the exothermic DTA effects at high temperatures.^{2,18} However, in the present case it is considered that the presence of impurities would have little or no effect, given the low proportion present in the kaolinite used coupled with the elimination of impurities coming from the aluminium alloys, which was checked using chemical analytical methods. It is worth noting here that the formation of such exothermic DTA peaks (mullite nuclei and/or spinel) is most likely due to the release of energy associated with the Al ions transforming to a more stable sixfold coordination, facilitating the formation of mullite, as proposed previously by Sanz *et al.*⁴ and more recently by Sánchez-Soto *et al.*¹⁹ using other mullite precursors.

Further investigation on the formation of mullite under dynamic heating conditions was performed using a temperature controlled device from room temperature up to a maximum of 1000 °C by XRD (thermal diffractograms). These results proved useful in comparison to those previous obtained by DTA-TGA. The most interesting was when HMDA was employed in the chemical processing of mullite precursors. These results can be seen in Fig. 4. The XRD patterns at room temperature (original) and 300 °C show some kaolinite, quartz and an amorphous phase. Kaolinite patterns disappear after further dynamic heating, which is accounted for in the weight loss shown in the TGA-DTG diagrams and the associated endothermic DTA effect (Fig. 3). There is also a large volume change attributed with the conversion of the powder with the organic compound to a ceramic powder. Low-crystalline mullite X-ray patterns can be detected after dynamic

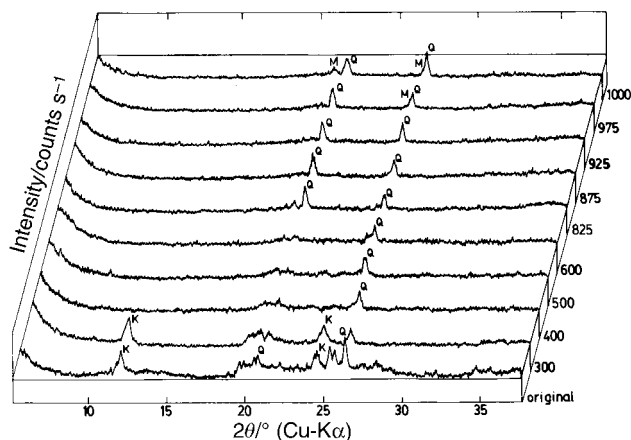


Fig. 4 XRD thermal diffractograms of mullite precursor sample obtained using HMDA. K=Kaolinite; Q=Quartz; M=Mullite.

heating at 975 °C (Fig. 4), *i.e.* when the characteristic exothermic DTA effect is observed with no weight loss (Fig. 3).

Thermal treatments of the pressed powders in air were performed to produce mullite from the reaction between amorphous silica, produced from metakaolinite decomposition, and aluminium oxide. This formation of mullite is accompanied by (meta)kaolinite decomposition. It is assumed that a similar reaction pathway, as proposed in the literature,^{5-7,10,11} accounts for the mullite formation using (meta)kaolinite–alumina mixtures by reaction sintering. This process involves the formation of primary mullite from (meta)kaolinite decomposition at temperatures close to 1300 °C, and at higher temperatures, the formation of secondary mullite by a solution–precipitation mechanism.

Fig. 5 shows selected XRD diagrams which correspond to samples obtained using ammonium hydroxide or HMDA in

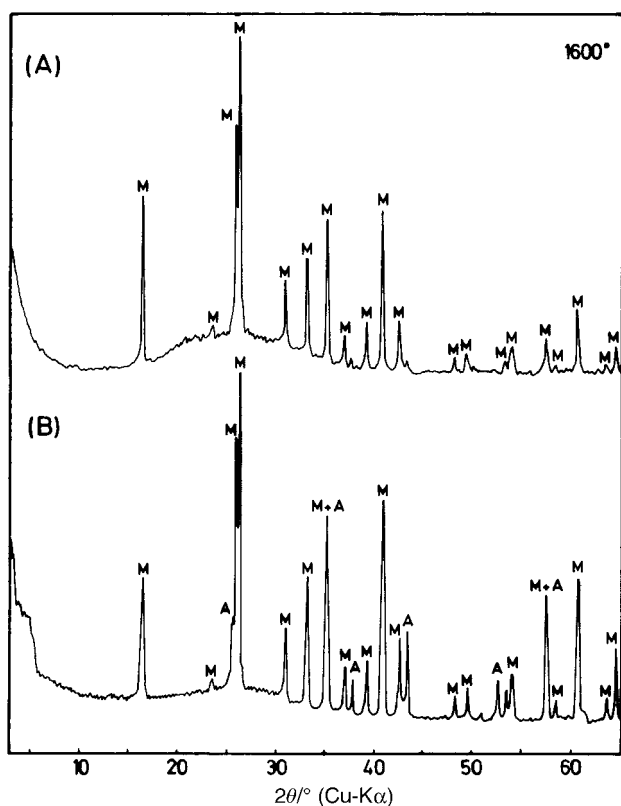


Fig. 5 XRD patterns of the precursor samples after thermal treatment in air at 1600 °C for 30 minutes: (A) sample processed using HMDA and (B) sample processed using ammonium hydroxide. M=Mullite (JCPDS card 15-776) and A=α-alumina (JCPDS card 10-173).

the precipitation processing step, as described above, and fired at a temperature of 1600 °C for 30 minutes. The formation of mullite is achieved, with α-alumina (corundum) remaining, which is indicative of using ammonia as a precipitating agent. The formation of α-alumina is produced from the solid-state transformation of γ-Al₂O₃. Thus, it is remarkable that mullite is produced in higher yield when HMDA was employed to produce the precipitation of aluminium hydroxide from aluminium salts than when ammonium hydroxide was used. Firstly, we could explain this result by taking into account the nature of HMDA, an organic compound which is able, in certain arrangements, to intercalate into the interlayer space of aluminosilicates,^{20,21} and thus participate in solid-state reactions favoured by thermal treatment and temperature increase until complete loss by oxidation at 600 °C. An alternative explanation is the formation of some kind of bond between the kaolinite layer, the amorphous phase containing aluminium oxide, and HMDA as coupling agent. According to the literature,²²⁻²⁴ despite the wide abundance of kaolinite in nature, it has been investigated significantly less than, for example, smectite clays as a precursor mineral for new organomineral materials. This is presumably due to the difficulty in expanding the interlayers of kaolinite as compared to other expandable layered materials. However, studies of chemically modified kaolinite²⁵ show that it is possible to modify the interlayers of this silicate with methanol by first expanding the interlayers with chemical agents, such as DMSO or NMF, and then treating them at high temperatures (>200 °C). Thus, the grafting of organic groups onto the interlayer aluminol surface of kaolinite is made possible. A previous paper reported results under adequate conditions using other aluminosilicates and alkylamines.²⁶ However, intercalation was produced in an indirect chemical way. This demonstrates the feasibility of intercalation reactions and grafting of organic groups under certain conditions.^{25,26}

In the present case, organic groups could be attached to the hydroxide surface of kaolinite (interlayer aluminol surface) through a condensation reaction whereby Al–O–C and/or Al–O–N bonds are involved. To some extent these could also be formed or favoured by thermal treatment. This is not the case, however, when ammonium hydroxide is employed in the precipitation step of aluminium hydroxide (Fig. 1). It is also suggested in this particular case that the diamine HMDA could also bond with reactive aluminium oxy-hydroxide which is precipitated in the kaolinite aqueous suspension. The reaction would also involve a simple dispersion effect of this organic chemical on the surface of kaolinite particles. The effect of the first stages of grinding kaolinite which induced random translations along the *b*-axis of the silicate layer may also favour all these processes.

It is also assumed that the formation of a secondary mullite, *i.e.* the reaction α-alumina–(meta)kaolinite, is produced at lower temperatures, being accelerated by the effect of eutectic liquid formation in the SiO₂–Al₂O₃ binary system at *ca.* 1587 °C.¹⁰ In this respect, it is reported¹⁰ that the reaction of α-alumina with kaolinite initiated at about 1250 °C, increases in speed from 1600 °C and beyond. This indicates the strong effect of the eutectic liquid formation in this system at *ca.* 1587 °C. Consequently, both effects are favourable using HMDA as a precipitating agent and as a coupling agent; they compare very favourable to using ammonium hydroxide. In relation to this, under slightly different conditions, the attack of a silicate network by aluminium cations was reported.¹⁷ The use of chemical agents (urea)¹⁷ as base generators, instead of sodium or ammonium hydroxide, should simplify the synthesis of reactive mullite precursors because it (a) avoids local excess base, and (b) increases the yield of hexacoordinated aluminium atoms in local structures similar to those present in kaolinite. This seems in accordance with the present results. Thus, as compared with ammonium

hydroxide used in the precipitation step, the advantageous effects of HMDA can be observed, and therefore mullite is formed as a single phase (Fig. 5).

SEM has been applied to study the mullite and mullite-based composites obtained during this chemical processing route. Fig. 6 shows the fine porous microstructure of the mullite body, obtained using HMDA as precipitating agent. It has the typical elongated morphology of mullite crystals, which was revealed after HF chemical etching. On the other hand, the presence of corundum (α -alumina) grains and mullite crystals was observed in the sample obtained using ammonium hydroxide in the precipitation processing step. This is in agreement with the phase analysis by XRD (Fig. 5). The presence of α -alumina grains and elongated mullite crystals was studied using energy dispersive X-ray spectroscopy and confirmed using electron diffraction. These microstructures, the development of crystalline phases, and the thermal evolution all suggest that mullitization occurred *via* a similar characteristic mechanism, as stated previously in the literature.^{5-7,10,11}

Flexural strength measurements of fired samples were performed at room temperature using the four points bending test. Table 1 shows some selected results of mullite samples obtained by this wet processing method. These results showed relatively low values with a minimum of 16.45 MPa after firing at 1550 °C in air using ammonium hydroxide as precipitating agent, and a maximum of 48.68 MPa after firing at 1600 °C using HMDA. The increased porosity, as will be shown later, could be the main cause of these low strength values. The flexural strength increases with the sintering temperature of the samples, and the use of kaolinite sample B [indicated as K(B) in Table 1] of lower particle size than A [indicated in Table 1 as K(A)] of relatively higher surface area. Moreover, the present results suggest that: (1) the use of HMDA results in samples with higher flexural strength, as compared with the use of ammonium hydroxide in the processing step of precipitation, at the same firing temperature; (2) the use of kaolinite samples with lower particle sizes (sample B) and higher surface area leads to materials with better strength, and furthermore (3) the presence of minority metal components in the Al alloy and/or the kaolinite sample does not seem to have a significant influence on the formation of mullite and on the mechanical properties of the fired materials.

The Hg intrusion porosimetry tests indicated that the materials obtained after firing are porous. The mullite materials obtained using HMDA (Fig. 6) show a drop in porosity values from 51.73 vol% after firing at 1550 °C in air to 44.98 vol% after firing at 1600 °C in air. This difference is assumed to be due to a firing effect of progressive sintering. The porosity values of mullite materials obtained using ammonia were similar to those obtained using HMDA, but the respective pore size distributions were distinct. According to all these results, the fired materials could have potential applications as ceramic substrates, catalytic supports, filters and isolating materials used at high temperatures as thermal barriers.

Conclusions

From these results the feasibility of using HMDA as a precipitating agent, in the proposed chemical processing route

Table 1 Flexural strength (σ_f) results of fired samples in air

Sample ^a	Firing temperature/°C	σ_f /MPa
K(B)HMDA	1600	48.68
K(B)HMDA	1550	21.63
K(A)HMDA	1600	40.21
K(B)NH ₄ OH	1600	34.72
K(B)NH ₄ OH	1550	16.45

^aObtained as described in experimental section (see the text).

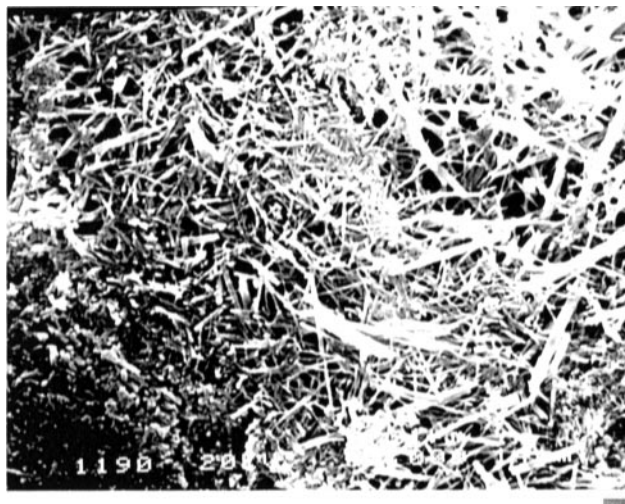


Fig. 6 SEM micrograph of a porous mullite body obtained after firing at 1600 °C the precursor obtained using HMDA, after HF chemical etching. Bar = 1 μ m.

for mullite preparation, has been demonstrated. The use of HMDA as a base precipitating agent as compared to ammonium hydroxide has desirable consequences as described in this work. The preparation of mullite as a single phase with a characteristic microstructure and enhanced flexural strength results in ceramic porous bodies (porosity *ca.* 45–50 vol%) by firing at 1550–1600 °C for 30 minutes, and is very favourable. The action of HMDA as an organic coupling chemical agent to modify the kaolinite layers and aluminium hydroxide is not clear, and is a matter for further research. On the other hand, the use of ammonium hydroxide as base precipitating agent produces a composite α -alumina–mullite by firing the precursor for 30 minutes at 1600 °C. This suggests a higher refractory tendency than for single-phase mullite alone. The resultant mullite materials as described in this paper could have potential applications as refractories, substrates, filters and isolating materials.

It is also to be pointed out that this route has implications for the recycling of aluminium metal wastes, and is a possible alternative to remelting. This may prove interesting in ceramic engineering and materials science. However, additional investigation into the above processing route is necessary, and is now in progress. The results will be a matter for future reports. Research may prove interesting and useful in establishing the appropriate relationships between processing variables, microstructure and properties.

Acknowledgements

This work was supported by CICYT (Ministry of Education and Science of Spain) through research project referenced MAT96-0507. The authors thank the anonymous reviewers whose comments greatly improved this paper. The authors wish to dedicate this work to Professor Dr Salvador de Aza for his vast contribution to the study of mullite formation and the science of ceramic processing.

References

- 1 W. D. Johns, *Mineral. Mag.*, 1953, **30**, 186; G. W. Brindley and M. Nakahira, *J. Am. Ceram. Soc.*, 1959, **42**, 311; G. W. Brindley and M. Nakahira, *J. Am. Ceram. Soc.*, 1959, **42**, 319.
- 2 J. Lemaitre, M. Bulens and B. Delmon, *Proc. Int. Clay Conf.* 1975, 1976, 539.
- 3 B. Sonuparlak, M. Sarikaya and I. A. Aksay, *J. Am. Ceram. Soc.*, 1987, **70**, 837; P. J. Sánchez-Soto, I. Sobrados, J. Sanz and J. L. Pérez-Rodríguez, *J. Am. Ceram. Soc.*, 1993, **76**, 3024;

- P. J. Sánchez-Soto and J. L. Pérez-Rodríguez, *Bol. Soc. Esp. Ceram. Vidrio*, 1998, **37**, 285.
- 4 J. Sanz, A. Madani, J. M. Serratos, J. S. Moya and S. de Aza, *J. Am. Ceram. Soc.*, 1988, **71**, C418.
 - 5 J. A. Pask and A. P. Tomsia, *J. Am. Ceram. Soc.*, 1991, **74**, 2367; H. Schneider, K. Okada and J. A. Pask, *Mullite and Mullite Ceramics*, Wiley, Chichester, 1994.
 - 6 S. Somiya, R. F. Davis and J. A. Pask, *Mullite and Mullite Matrix Composites*, Vol. 6, *Ceramics Transactions*, The American Ceramic Society, Ohio, 1990.
 - 7 I. A. Aksay, D. M. Dabbs and M. Sarikaya, *J. Am. Ceram. Soc.*, 1991, **74**, 2343.
 - 8 M. D. Sacks, H. W. Lee and J. A. Pask, *Mullite and Mullite Matrix Composites*, Vol. 6, *Ceramics Transactions*, The American Ceramic Society, Ohio, 1990, pp. 167–207.
 - 9 R. F. Davis and J. A. Pask, *J. Am. Ceram. Soc.*, 1972, **55**, 525.
 - 10 K. C. Liu, G. Thomas, A. Caballero, J. S. Moya and S. de Aza, *J. Am. Ceram. Soc.*, 1994, **77**, 1545; K. C. Liu, G. Thomas, A. Caballero, J. S. Moya and S. de Aza, *Acta Metall. Mater.*, 1994, **42**, 489; P. Pena, J. Bartolomé, J. Requena and J. S. Moya, *J. Phys. IV*, 1993, **3**, 1261.
 - 11 J. Requena, J. F. Bartolomé, J. S. Moya, S. de Aza, F. Guitián and G. Thomas, *J. Eur. Ceram. Soc.*, 1996, **16**, 249.
 - 12 F. H. Norton, *Fine Ceramics, Technology and Applications*, McGraw-Hill, NY, 1970.
 - 13 S. Somiya and Y. Hirata, *Am. Ceram. Soc. Bull.*, 1991, **70**, 1624; K. Okada, N. Otsuka and S. Somiya, *Am. Ceram. Soc. Bull.*, 1991, **70**, 1633.
 - 14 N. Claussen, T. Le and S. Wu, *J. Eur. Ceram. Soc.*, 1989, **5**, 29;
 - J. Brandt and R. Lundberg, *Third Euroceramics*, ed. P. Durán and J. F. Fernández, Faenza Editrice Ibérica S.L., 1993, Vol. 1, p. 169.
 - 15 M. D. Sacks, N. Bozkurt and G. W. Scheffele, *J. Am. Ceram. Soc.*, 1991, **74**, 2428; M. D. Sacks, Y.-J. Lin, G. W. Scheffele, K. Wang and N. Bozkurt, *J. Am. Ceram. Soc.*, 1996, **79**, 2897.
 - 16 R. M. Laine, D. R. Treadwell, B. L. Mueller, C. R. Bickmore, K. F. Waldner and T. R. Hinklin, *J. Mater. Chem.*, 1996, **6**, 1441.
 - 17 I. Jaymes, A. Douy and D. Massiot, *J. Am. Ceram. Soc.*, 1995, **78**, 2648.
 - 18 M. Bullens and B. Delmon, *Clays Clay Miner.*, 1977, **25**, 271; S. M. Johnson, J. A. Pask and J. S. Moya, *J. Am. Ceram. Soc.*, 1982, **65**, 31.
 - 19 P. J. Sánchez-Soto, J. L. Pérez-Rodríguez, I. Sobrados and J. Sanz, *Chem. Mater.*, 1997, **9**, 677.
 - 20 B. K. G. Theng, *The Chemistry of Clay-Organic Reactions*, Adam Hilger, London, 1974, Ch. 6, pp. 239–260.
 - 21 *Intercalation Chemistry*, ed. M. S. Wittingham and A. J. Jacobson, Academic Press, New York, 1982.
 - 22 D. M. C. MacEwan and M. J. Wilson, in *Crystal Structures of Clay Minerals and Their X-ray Identification*, ed. G. W. Brindley and G. Brown, Mineralogical Society, London, 1984, p. 197.
 - 23 J. A. Rausell-Colom and J. M. Serratos, in *Chemistry of Clays and Clay Minerals*, ed. A. C. D. Newman, Mineralogical Society, London, 1987, p. 371.
 - 24 H. H. Murray, in *Hydrous Phyllosilicates*, ed. S. W. Bailey, Mineralogical Society of America, Washington DC, 1988, p. 67.
 - 25 J. J. Tunney and C. Detellier, *Chem. Mater.*, 1993, **5**, 747; J. J. Tunney and C. Detellier, *J. Mater. Chem.*, 1996, **6**, 1679.
 - 26 M. A. Avilés, A. Justo, P. J. Sánchez-Soto and J. L. Pérez-Rodríguez, *J. Mater. Chem.*, 1993, **3**, 223.