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Single-phase and Diphasic Aerogels and Xerogels of Mullite: Preparation and Characterization

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Abstract

Single-phase mullite composition gels have been synthesized using tetraethoxysilane [$Si(OC_2H_5)_4$] and aluminum nitrate nonahydrate as precursors. Diphasic mullite gels have been prepared using colloidal silica and boehmite as precursors. Xerogels and aerogels of both the above gels have been obtained by ordinary drying in air at 60°C and critical point drying in methanol, respectively. Single-phase xerogels show an intense exothermic peak at about 980°C while their counterparts, aerogels, do not show any detectable exotherm by differential thermal analysis (DTA). These results suggest that the structure of single phase gels changed during critical point drying and the structural changes were investigated by solid-state ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy. No differences between diphasic xerogels and aerogels could be detected by DTA because there was little or no effect of drying on the discrete silica and alumina phases. The tetrahedral coordination of Al in single-phase mullite gel changed to octahedral coordination as detected by MAS NMR during critical point drying, which suggests that the alumina component segregated. Both single-phase and diphasic aerogels of mullite composition showed very high surface areas in the temperature range 1000–1400°C and these may be useful for high temperature catalytic applications.

Introduction

The concept of diphasic nanocomposites for the synthesis of mullite, $Al_6Si_2O_{13}$ and other compositions was first introduced by us.[1–3] The diphasic mullite gels led to enhanced densification at very low temperatures.[4–5] The mechanism of nucleation and densification in single and diphasic gels has been studied by numerous investigators.[6–12] Solid-state nuclear magnetic resonance studies of ^{27}Al and ^{29}Si have revealed that single-phase gels made from aluminum nitrate and tetraethoxysilane are mixed on an atomic to molecular level while the diphasic gels are mixed on a nanometre scale.[13–14]

The single-phase gels crystallize to mullite at lower temperatures than the diphasic gels. The rapid crystallization of mullite in the former gels is not conducive for densification while the diphasic gels led to enhanced densification apparently due to densification and crystallization in a very narrow temperature range.[15] The enormous worldwide interest in mullite for high temperature structural applications is due to its high creep and thermal shock resistance as well as its high strength at very high temperatures. For extremely good mechanical properties, the achievement of full densification with fine microstructure and without any glassy phase is imperative. This is the reason why there are numerous studies on mullite densification. The study of porous mullite ceramics for high temperature catalysis, separations, etc., has, however, been neglected. Thus the objectives of this study are (1) to prepare and characterize single-phase and diphasic aerogels and xerogels of mullite and (2) to characterize the porosity characteristics of these mullite gels after sintering to high temperatures.

Experimental

Preparation of mullite single-phase gels

Mullite single-phase gels and diphasic gels were made by the procedure used previously.[1,4,5] Aluminum nitrate nonahydrate (56·16 g) was mixed with 95% ethyl alcohol (75 ml) and stirred for 1 h. Tetraethylorthosilicate (TEOS) (11·1 ml) was added and the sol was poured into tubes and kept at 60°C until gelation. After gelation, gels were exchanged in methanol for 4–12 days more. Aerogels were made by critical point drying and xerogels were made by drying at 60°C.

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Preparation of mullite diphasic gels

Mullite diphasic gels, with excess Al_2O_3 (nominal composition: 86·5% Al_2O_3–13·5% SiO_2) were made by mixing boehmite (39·34 g) with 160 ml of distilled water for 30 min. Concentrated nitric acid was added to bring the pH to 3. Commercial colloidal silica (Ludox AS40) was added (12·12 g) and the sol was stirred. The sol was poured into glass tubes and gelled. After gelation the diphasic gels were exchanged with methanol. Diphasic mullite aerogels and xerogels were made in the same fashion as those of single-phase mullite gels.

Aerogel preparation by supercritical drying

Both the single-phase and diphasic mullite gels were aged in methanol at room temperature for 4–12 days to exchange residual water out of the pores of the gels. Aerogels were produced by methanol or ethanol critical point drying at 260 or 270°C and 8·27 MPa in a 50 ml Hastalloy C autoclave (Autoclave Engineers). Both single-phase and diphasic mullite gels were run simultaneously so they would have identical drying conditions. The two types of gel in Pyrex tubes were critical point dried in each 4 h run of the autoclave. Two tubes were placed in the autoclave, and 15 ml of alcohol was added to maintain alcohol vapour pressure during the heating period to prevent the premature loss of pore fluid from the gel. An anti-seize compound (Permatex Industrial anti-seize lubricant) was added to the threads, and the vessel was sealed. The autoclave was pre-pressurized with nitrogen to 8·27 MPa, and a three-stage program was activated on the Omega CN 2041 programmable temperature controller. The first stage heated the autoclave from room temperature to 260 or 270°C over 3 h. The pressure was released manually every 15–30 min to maintain the autoclave pressure in the range 8·27 to 8·96 MPa. For the second stage, the pressure was maintained at 8·27 MPa and the temperature was kept at 260 or 270°C. After 15 min into this second stage, the argon valve was opened and the autoclave exhaust valve was opened slightly to purge the supercritical methanol from the chamber. After 15 min of purging, the pressure on the autoclave vessel was released and the temperature was allowed to decrease slowly.

Sintering of aerogels

Sintering was carried out on unground samples. Each individual aerogel sample was sub-sampled for nitrogen BET analysis. Then samples of about 0·1 g each were removed for sintering. The aerogel and xerogel samples were sintered at 900, 1000, 1200 and 1400°C for 2 h. A Lindberg programable furnace was used with a heating rate of 2°C min^{-1}; cooling rates were no greater than 2°C min^{-1}. Samples were weighed before and after sintering to determine weight loss. Sintering was carried out in platinum trays with platinum foil covering the samples.

Characterization of aerogels

The aerogels were characterized to determine thermal stability, analyse the phases present, and measure textural properties. BET nitrogen adsorption analysis was the primary characterization technique for textural properties.

Powder X-ray diffraction of variously treated aerogels and xerogels

Powder X-ray diffraction (XRD) was carried out using a Scintag X-ray diffractometer with Ni-filtered CuK_α radiation. Powders were dispersed on glass slides using ethanol. The diffraction data were analysed using standard commercial software and the standard diffraction data provided by the Joint Committee on Powder Diffraction Standards (JCPDS).

Differential thermal analysis

The xerogels and aerogels were characterized by differential thermal analysis (DTA) with a Perkin–Elmer DTA 1700 instrument using a heating rate of 10°C min^{-1} in air.

^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy

The mullite aerogel and xerogel samples were characterized by ^{27}Al MAS NMR spectroscopy using a SDS 360 instrument operating at a Larmor frequency of 94·669 MHz. The samples were spun at 8·5 to 10·5 kHz and the chemical shifts are reported as ppm with respect to $[Al(H_2O)_6]^{3+}$ as an external standard.

Scanning electron microscopy (SEM)

An ISI DS-130 scanning electron microscope was used for determining the particle size and morphology of the as-prepared and sintered single-phase and diphasic aerogels.

BET nitrogen adsorption analysis

Surface area analysis and pore size distribution were determined by multi-point BET analysis and by adsorption and desorption isotherms of nitrogen using an Autosorb-1 (Quantachrome, Syosset, New York). As-prepared aerogels and sintered aerogels were ground gently in an agate mortar with a pestle. Powders (0·04 to 0·08 g) were weighed and transferred to glass BET tubes of known weight. The samples were degassed at 60°C for 30 min or longer. The samples were weighed in

BET tubes and true sample weights were calculated, following standard procedures.

Twenty-point adsorption isotherms and 20-point desorption isotherms were obtained for each sample. The multipoint BET surface area was determined using up to eight adsorption points. Pore size distribution was determined using desorption $D(v)dr$ plots. For comparison purposes, a numerical pore size figure was determined by measuring the centre of the peak at half of the maximum peak amplitude.

Results and Discussion

Differential thermal analysis curves of aerogels and xerogels are shown in Fig. 1. The single-phase xerogel shows an intense exotherm at about 980°C (Fig. 1(A)), as expected based on previous studies, due to atomic or molecular scale mixing of alumina and silica components.[13,14] The single-phase aerogel, however, shows no exotherm (Fig. 1(B)) in the high temperature range 500–1200°C in a similar way to that of a diphasic mullite gel (Fig. 1(C)). The absence of an exotherm at 980°C in single-phase mullite aerogel was unexpected, but it was expected in the case of diphasic mullite aerogel, the latter being based on previous studies of diphasic xerogels.[1] Thus, the single-phase mullite aerogel is showing a thermal behaviour similar to that of a diphasic aerogel or xerogel. The above implies that the single-phase mullite gel may have altered during methanol critical point drying to a type of diphasic gel, probably due to the segregation and crystallization of alumina phase.

This hypothesis was tested by powder XRD and ^{27}Al MAS NMR spectroscopy. The as-prepared single-phase xerogel and aerogel show somewhat similar XRD patterns (not shown) with little or no crystallinity and, thus, no difference between the two can be detected. Boehmite could not be detected in the as-prepared aerogel by XRD. The as-prepared diphasic aerogel shows boehmite which is one of the starting phases. The amorphous silica sol cannot be detected by XRD, as expected. The segregation and crystallization of alumina phase to boehmite-like phase during critical point drying of single-phase mullite gel at 270°C is uncertain based on these XRD studies. For this reason, ^{27}Al MAS NMR spectra of the three different gels (Fig. 2) were obtained to detect any differences. The single-phase xerogel (Fig. 2(A)) shows two ^{27}Al resonances, one at 54·56 ppm and another at 0·449 ppm which can be attributed to the tetrahedral and octahedral

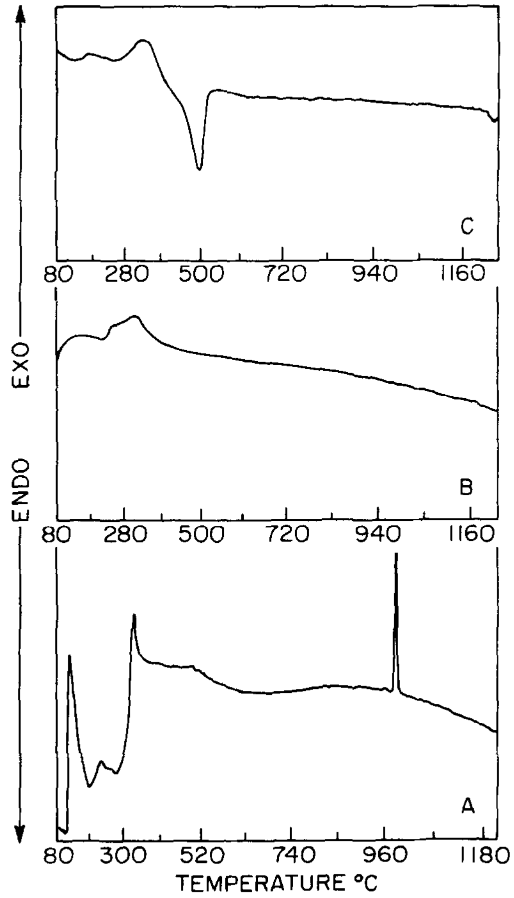

Fig. 1. Differential thermal analysis curves of (A) single-phase mullite xerogel, (B) single-phase mullite aerogel and (C) diphasic mullite aerogel.

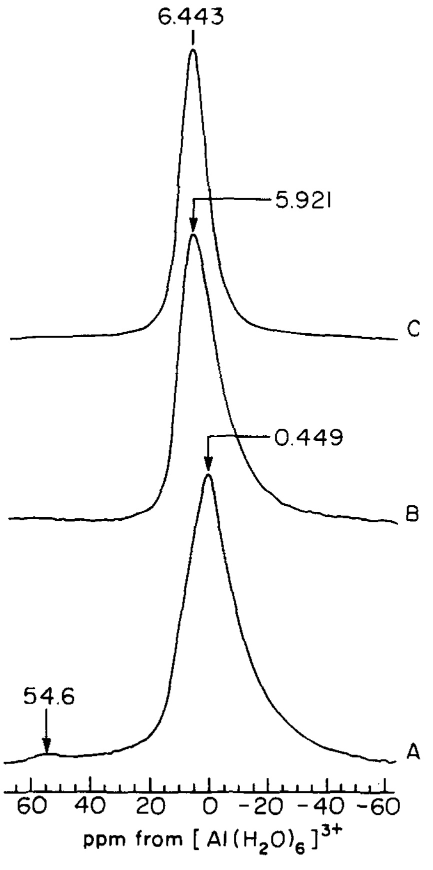

Fig. 2. ^{27}Al MAS NMR spectra of (A) single-phase mullite xerogel, (B) single-phase mullite aerogel and (C) diphasic mullite aerogel. Since these chemical shifts are not corrected for quadrupolar effects, the decimals have no significance.

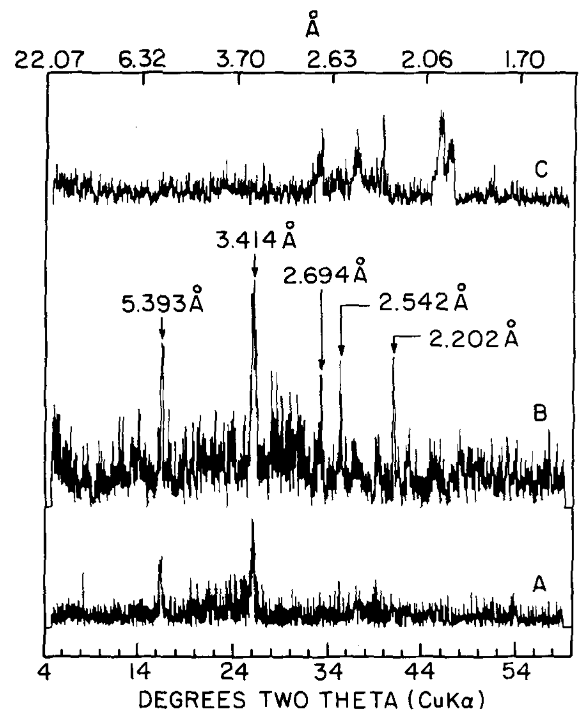

Fig. 3. Powder X-ray diffraction patterns of different mullite gels after DTA run to 1250°C: (A) single-phase xerogel shows mullite peaks, (B) single-phase aerogel shows mullite peaks and (C) diphasic aerogel shows delta alumina peaks.

coordinations, respectively. The tetrahedral coordination of Al implies that part of the Al is in the nearest neighbour environment of silicon due to atomic-scale mixing. When the single-phase gel was dried under supercritical conditions to prepare the aerogel, the ^{27}Al resonance at 54·56 ppm disappeared and only the octahedral ^{27}Al resonance at 5·92 ppm was present (Fig. 2(B)). The diphasic aerogel shows only one resonance at 6·44 ppm (Fig. 3(C)) representing all Al in octahedral coordination because boehmite is one of the starting phases which has Al in octahedral coordination only. Thus the ^{27}Al MAS NMR data show that the alumina component segregated during critical point drying of the single-phase gel to form a boehmite-like phase. These results are supported by the work of Mizushima and Hori,[16] who showed that small boehmite crystals recrystallized to larger crystals during long (72 h) critical point drying of boehmite aerogels.

Powder XRD results of single-phase xerogel and aerogel and diphasic aerogel after heat treatment to 1250°C in the differential thermal equipment shows the formation of mullite in both the single-

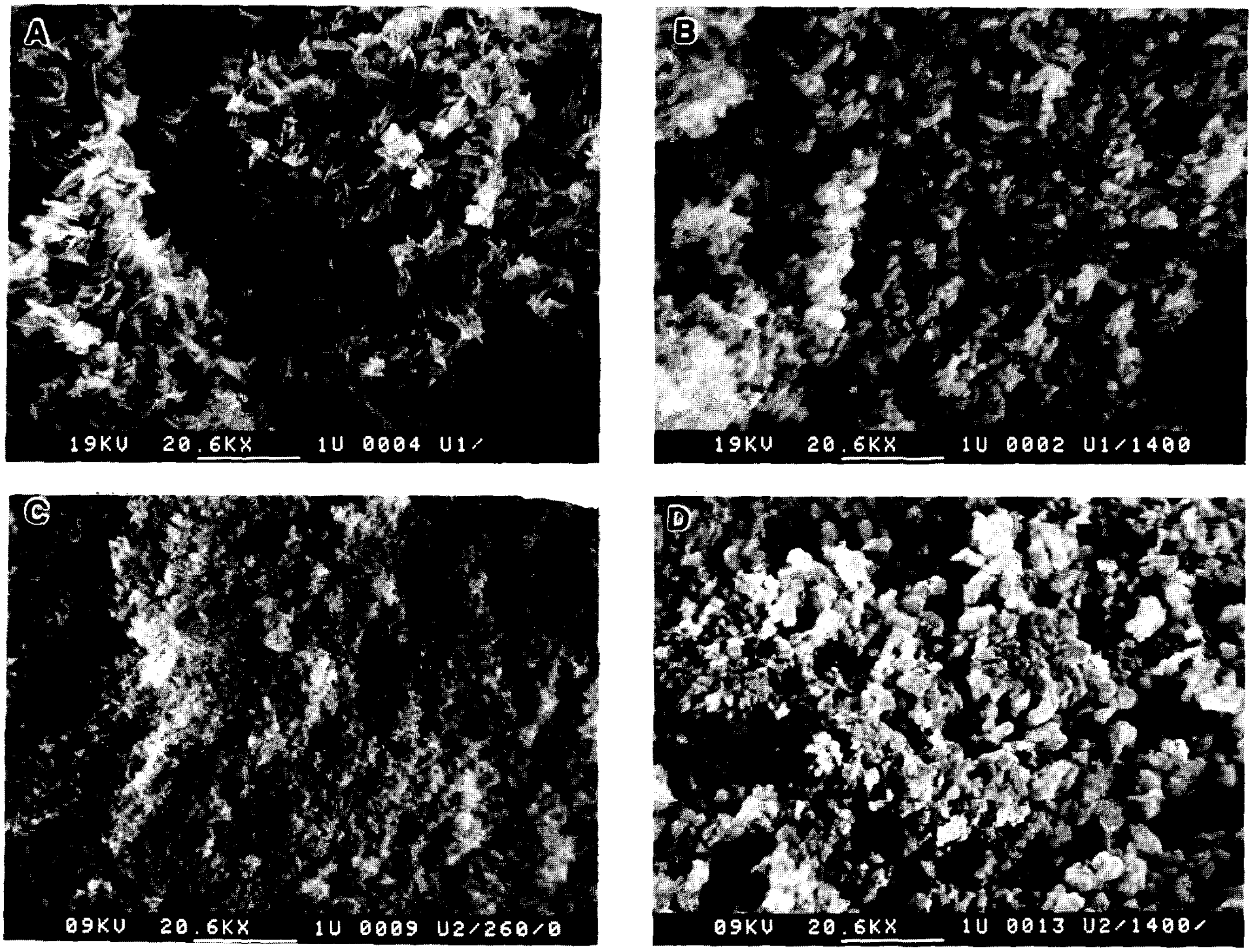

Fig. 4. Scanning electron micrographs of mullite gels: (A) as-prepared single-phase gel, (B) single-phase gel sintered at 1400°C/2 h, (C) as-prepared diphasic gel and (D) diphasic gel sintered at 1400°C 2 h.

Table 1. Surface area and pore sizes of as-prepared and sintered single-phase and diphasic aerogels of mullite composition

	As prepared, 260°C		*As prepared, 270°C*		*Sintered*[a] *at 1000°C, 2 h*		*Sintered*[a] *at 1200°C, 2 h*		*Sintered*[a] *at 1400°C, 2 h*	
	Surface area $(m^2 g^{-1})$	*Pore radius (nm)*	*Surface area* $(m^2 g^{-1})$	*Pore radius (nm)*	*Surface area* $(m^2 g^{-1})$	*Pore radius (nm)*	*Surface area* $(m^2 g^{-1})$	*Pore radius (nm)*	*Surface area* $(m^2 g^{-1})$	*Pore radius (nm)*
Single phase	334	1·8; 17[b]	434	2·1; 13[b]	309	1·8; 15[b]	66	nd[c]	27	1·3; 4[b]
Diphasic	152	13	180	22	148	1·4	93	20	15·7	1·3; 3.2; 26[b]

[a] Sintered samples were critical point dried at 260°C.

[b] Two or more numbers indicate different pore radii in the same gel in order of their abundance as determined by the areas of peaks from pore-size distribution plots.

[c] Not determined.

phase xerogel and aerogel. The diphasic aerogel, however, shows only delta alumina under the dynamic heating condition (10°C min^{-1}) of the DTA. These results show that the alteration of single-phase gel to diphasic gel during critical point drying can be detected by both DTA and ^{27}Al MAS NMR but not by XRD. Thus DTA and ^{27}Al MAS NMR techniques are more sensitive than XRD in identifying phase segregation in mullite gels.

The scanning electron micrograph of the as-prepared single-phase mullite aerogel shows porosity and an interesting acicular morphology (Fig. 4(A)). This aerogel sample sintered to 1400°C also shows needle-shaped mullite crystals (Fig. 4(B)). The as-prepared diphasic gel shows porosity and a very fine grained structure (Fig. 4(C)) as expected, because of the two mixed sols. The sintered diphasic porous mullite shows equiaxed, submicrometre grains (Fig. 4(D)). All the mullite composition gels showed mullite by XRD after sintering at 1400°C.

The textural properties of the as-prepared and sintered single-phase and diphasic mullite gels are shown in Table 1. The different aerogels of mullite retain high surface areas in the temperature range 1000–1400°C, which suggests that these can be tailored for high-temperature catalytic applications.

Conclusions

Both single and diphasic aerogels of mullite composition exhibit high surface areas after sintering in the temperature range 1000–1400°C. Segregation of the alumina component occurred during critical point drying of single-phase mullite composition gels. Sintered aerogels of mullite composition may be useful for high temperature catalytic applications.

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