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Characterization of co-precipitated Al_2O_3–SiO_2 gels

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Aluminum nitrate and tetraethyl orthoxysilane were used as starting materials. They were mixed at different ratios ranging from 1.8 to 4.8 (Al^{3+}/Si^{4+}) and dissolved in ethyl alcohol. The pH of the reaction solution was also varied by the addition of ammonium hydroxide at a range of 8.3 to 10.4. Experiments were carried out at 25 and 60° C. In each case the materials were hydrolysed to a colloidal solution which was then filtrated and the resulting colloids retained on the filter as a gel which after drying at 110° C became a xerogel. The xerogels then were characterized by BET, SEM/TEM, and XRD/XRF.

Of all the factors studied the pH of the reaction mixture was found to have the greatest affect on the morphology of the crystalline phase in the xerogels. Fibrous pseudoboehmite was found at the lower pH values of 8.3 and bayerite was present at pH value greater than 9.5 and became the predominant species at pH values greater than 10.4. The Al^{3+}/Si^{4+} ratios and the reaction temperature both affected the crystallinity of the xerogels but to a much lesser degree than did the pH.

1. Introduction

Mullite ($3Al_2O_3 \cdot 2SiO_2$), a two-component system ceramic, is difficult to synthesize by conventional methods as a high-purity powder. It can be obtained through sol–gel processes [1], and can be greatly improved by controlling some reaction conditions [2, 3], notably the homogeneous mixing of Al_2O_3 and SiO_2 and controlling of the impurities present.

The chemical reaction of the sol–gel process is rather complex. It is strongly dependent on the used starting materials. Reaction parameters such as the pH, reaction temperature, concentration and types of solvent, and the catalyst involved in the reaction can also affect the results [4]. In the Al_2O_3–H_2O system, the crystalline phases are determined by the starting materials and reaction parameters [5]. The presence of additives and organic solvent influence the phase transformation of aluminium hydroxides [6]. Dynys *et al.* obtained fibrous pseudoboehmite by hydrolysing aluminium sec-butoxide in secbutanol and water solution [7]. Lamber obtained fibrous boehmite by direct hydration of the aluminium oxide films in distilled water [8]. However, non-fibrillar, plate-like pseudoboehmite gels had also been reported [6, 9]. Aluminium hydroxide was finely divided into spherical granules about 3.0 nm in diameter then combined into fibres [10]. On ageing, these flexible fibres lined up to form rectangular plates. The difference between pseudoboehmite and boehmite is the face of (002) spacing from 0.61 nm of boehmite to 0.66 to 0.67 nm of pseudoboehmite under XRD analysis [5]. On ageing in a mother liquor of a pH > 7 and with no alkali ions present, the pseudoboehmite will transfer to bayerite and nordstrandite via dissolution and recrystallization. Bayerite is the initial phase, while the formation of nordstrandite needs high $[OH^-]$ concentration [5]. Bayerite particles usually occur as somatoids [5].

There were few reports concerning the Al_2O_3–SiO_2–H_2O (mullite) system. The influence of silicon hydroxide was equivocal. Hirata *et al.* [11] synthesized mullite powder from Al_2O_3–SiO_2 xerogels using aluminium and silicon alkoxides as starting materials. They found that nordstrandite, bayerite and boehmite gel were formed under different conditions. The boehmite gel behaved as pseudoboehmite [12]. The infrared spectrometric investigation showed no Al^{3+}–Si^{4+} bond.

In the synthesis of high purity mullite powder, the crystalline phases presenting in the xerogel are critical [13], and the use of salts instead of metal alkoxides for hydrolysis reaction is more applicable [14]. This study will examine the formation and properties of Al_2O_3–SiO_2–H_2O (mullite) xerogels prepared by the hydration of aluminium salts and silicon alkoxides, using aluminium nitrate and tetraethyl orthoxysilane as starting materials.

2. Experimental procedure

2.1. Starting materials and processing

Aluminium nitrate ($Al(NO_3)_3 \cdot 9H_2O$)* and tetraethyl orthoxysilane (TEOS, $Si(OC_2H_5)_4$)† were used as starting material. They were mixed with different $[Al^{3+}]/[Si^{4+}]$ ratios, ranging from 1.8 to 4.8, and

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dissolved in 75 ml of ethyl alcohol* (each mixture weighed about 135 g). Each solution was stirred for 1 h till optically homogeneous [3] (starting solution) and added to an agitating NH_4OH solution (reaction solution) within 1.5 h. The Al^{3+} and TEOS of the starting solution hydrolysed and became a colloidal solution. The reaction solutions contained 0.65 to 4.28 N of NH_4OH. The selected reaction temperature was 25° C. Two additional samples were prepared at 60° C. The colloidal solutions were aged for 6 h and filtrated on a Buchner funnel. The precipitates were then cleaned by resuspending in distilled water and refiltrating and repeat three times. Dewatering of the precipitates was carried out in a drying oven at 110° C for 24 h and then the xerogels were obtained.

2.2. Properties

The shape and particle size of the xerogels were examined by using electron microscopy (SEM*, TEM†). Measurement of the specific surface area was carried out by the BET‡ method. Crystal phases were identified by XRD§ and SADP (selected area diffraction pattern) of TEM. The ratio of Al_2O_3/Al_2O_3 + SiO_2 were identified by the XRF¶ method [15].

3. Results and discussion

3.1. Effects of reaction pH

3.1.1. Phase transformation

In the hydrolysis of salts, the pH value of the aqueous solution played the most important role of all the factors affecting the properties of the xerogels [5]. Throughout the study, the behaviour of the Al_2O_3–SiO_2–H_2O system can be interpreted by two possibly independent systems: Al_2O_3–H_2O and SiO_2–H_2O. Both properties were affected by the pH value of the reaction solutions.

At room temperature (25° C), xerogels which were prepared from the starting solution of Al : Si = 3 : 1 (or identical to the stoichiometric mullite). Fig. 1 depicts the relationship between the Al_2O_3 contents and the pH values: The highest Al_2O_3 content appeared between pH 9.5 and 10.1, where the xerogels had the closest Al_2O_3–SiO_2 ratios to those of the starting solutions. Apart from this region the Al_2O_3 content decreased, especially at high pH (> 10.1) values the content fell drastically. Because the TEOS in the starting solution would be mostly hydrolysed on ageing [16] and the solubility of silicon hydroxide kept constant when pH < 10.5 [17], the Al_2O_3 content of the xerogels was mainly affected by the solubility of the aluminium hydroxide.

The mineral phases of the aluminium hydroxide were heavily influenced by the pH value of the mother solution [5]. However, the pH values for the presence of the pseudoboehmite and bayerite in this study are different from those obtained by other investigators [5, 12, 22]. At pH 8.3 the xerogel is as pseudoboehmite (Fig. 2), it appears at a pH value slightly lower than that obtained by Hirata *et al.* [11]. In Hirata's work the products at pH < 9.1 were amorphous aluminium hydroxides. As the pH increased to 9.5, bayerite was identified, although the pseudoboehmite was still the major phase. The amount of bayerite increases with an increase of pH from 9.5 to 10.4 and eventually the amount is greater than the pseudoboehmite as the pH is raised to 10.4. The abundance of pseudoboehmite at the pH between 8.3 to 9.5 may imply the prevalence of a topochemical reaction progressing in the solution [18]. In the amorphous crystalline transformation of aluminium hydroxides, a sufficiently high [OH] concentration (pH > 7) in the aqueous solution is generally employed to control the replacement of water by (OH) ions. This was concluded from the results of the formation of crystalline $Al(OH)_3$ in the ageing process of the Al_2O_3–H_2O system.

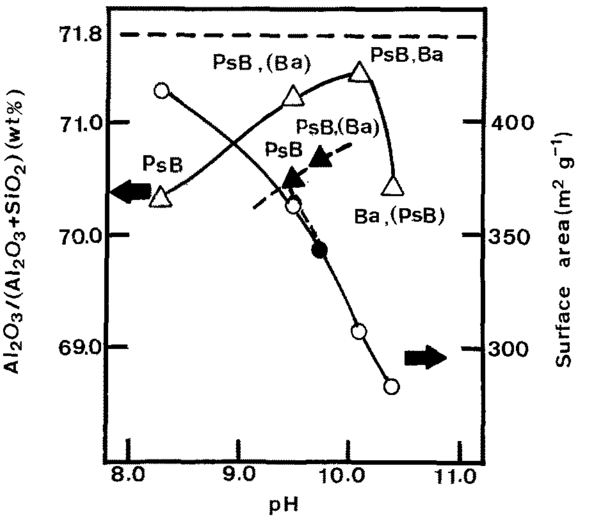

Figure 1 Variations of $Al_2O_3/(Al_2O_3$ + $SiO_2)$ and surface area of Al_2O_3–SiO_2 xerogels at different pH (at 25 and 60° C).

A topochemical reaction is explained to have taken place if an (OH) ion reacts topochemically with another (OH) ion rather than replacing a water molecule that surrounds the aluminium ions. This is also proposed as the mechanism for the formation of pseudoboehmite [19]. Pseudoboehmite may transfer to bayerite and nordstrandite if it remains under a mother liquor of pH > 7. Increasing the pH and temperature of the bath will accelerate their transformation. The pH values for this study was different from those used by other investigators who also used different starting materials (Table II). The pH for the transformation of pseudoboehmite to bayerite in this study was higher than that in pure aluminium hydroxides (pH > 7) [5]. It is also higher than that obtained in the solution of aluminium hydroxide and zirconium hydroxide (pH = 7.8 to 8.1) [20], but was lower than that found by Hirata *et al.* [11] (pH = 10.0) where aluminium alkoxide and silicon alkoxide were used as starting materials. The addition of silicon hydroxide in the study tended to enhance the (OH)–(OH) topochemical

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*SEM: Hitachi S-405A, Tokyo, Japan.
†TEM: JOEL JEM-200 STEM, Japan.
‡BET: Surface Area Analyser, Micrometric, Georgia, USA.
§XRD: Rigaku D/max IIIV, Tokyo, Japan.
¶XRF: Rigaku 3063, Osaka, Japan.

TABLE I The reaction condition and properties of Al_2O_3–SiO_2 xerogels

Sample	Reaction conditions			Properties of xerogels		
	pH	Temp.	$[Al^{3+}]/[Si^{4+}]$	Al_2O_3 %*	S.A.†	Phase‡
MA-25	8.3	25	3.3	70.3	413	PsB
MB-25	9.5	25	3.3	71.2	362	PsB, (Ba)
MC-25	10.1	25	3.3	71.4	306	PsB, Ba
MD-25	10.4	25	3.3	70.4	282	Ba, (PsB)
NMA-25	8.3	25	4.8	79.1	370	PsB
NMB-25	8.3	25	3.6	73.9	381	PsB
NMC-25	8.3	25	2.2	63.3	400	PsB
NMD-25	8.3	25	1.8	58.7	337	PsB
MB-60	9.5	60	3.3	70.5	363	PsB
MC-60	9.7	60	3.3	70.7	341	PsB, (Ba)

*Al_2O_3 % = $Al_2O_3/(Al_2O_3 + SiO_2)$ (wt %)

†S.A.: Surface area ($m^2 g^{-1}$)

‡PsB: Pseudoboehmite, Ba: Bayerite, ( ): minor

reaction in favour of the existence of pseudoboehmite instead of (OH)-H_2O replacement. As the presence of the organic additions can retard the formation of the crystalline phase and the recrystallization process of trihydroxide [6]. Possibly the incomplete removal of the organic additive may account for the pseudoboehmite → bayerite transformation not occurring until a pH > 9.5 was reached. The introduction of silicon-alkoxide, with its inherent ability as a liquid to be more ready mixed, the well mixing of the (Si^{4+}–Al^{3+}–H_2O) system may also play an important role. It is observed that the well mixing seems to prevent the dissolution-recipitation process which is provided by (OH) ion. Consequently a higher pH value would be needed for the pseudoboehmite → bayerite transformation. As bayerite is always present as the initial crystalline phase in Al-trihydroxides, which then transforms to nordstrandite when aged in a high pH solution. The absence of nordstrandite throughout this study may have resulted from the lower pH used, the interference caused by the existence of silicon compounds, or the insufficient aging period. Hirata [11], however, found that the nordstrandite was present at pH values greater than 10.9.

The silicon hydroxide in the xerogels exists as the amorphous phase under all conditions in this study. There was no sign of the crystalline phase identified in either the X-ray or the electron diffractographs (Figs 2 and 3).

3.1.2 Phase morphology

The shape of pseudoboehmite colloidal particle prepared at 25°C, pH = 8.3, was acicular to fibrillar in texture as previous reports [7, 8]. It is about 50 nm in length (Fig. 3a). The SADP was a large halo with diffused rings (Fig. 3b), representing the poor crystallinity of the pseudoboehmite. The ring was indexed to be $(2\,3\,1)_{\text{pseudoboehmite}}$, $d = 0.416$ nm. The bayerite formed at pH = 10.4 (25° C) was a plate-like irregular particle of varying size which generally ranged from 50 to 100 nm in its longest dimension (Fig. 3c). The SADP was a spot pattern with a halo at the centre, where a set of superlattice reflections were occasionally formed (Fig. 3d).

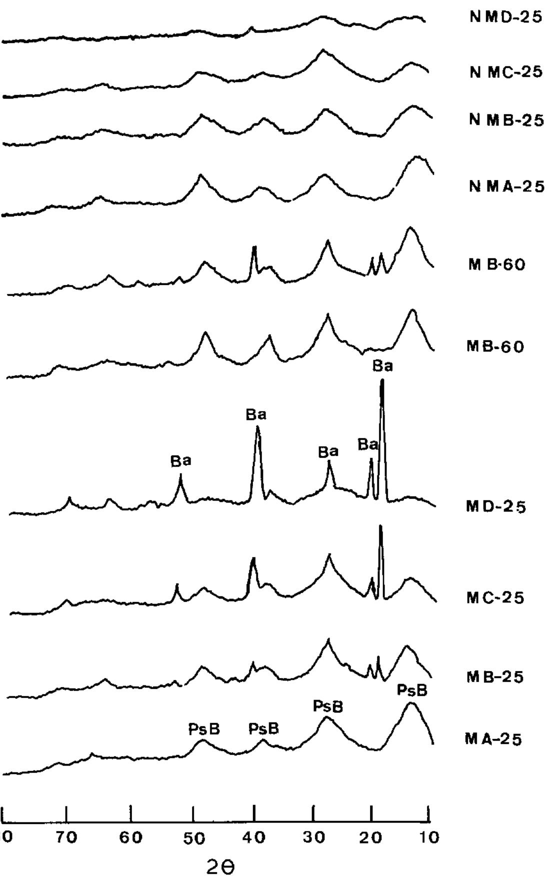

Figure 2 The X-ray diffractograms of Al_2O_3–SiO_2 xerogels at different reaction condition.

Both of the two phases were heavily flocculated. The reticulated pseudoboehmite was relatively uniform in size (800 to 1000 nm in length) and tended to be spherical. However, the bayerite was generally dendritic and irregular with the size of 100 to 700 nm. The silicon hydroxide was not found under TEM observation.

Under SEM observation the xerogel was constructed with the piled up plates or granulars. Its appearance was colloform nodular with varying sizes of constituent individuals, depending on the preparation conditions. The xerogel prepared at 25° C, pH = 8.3 was readily recognized by its thin tooth-like plates ($d = 3 \sim 5\,\mu$m) and slightly rounded surface with "cockscomb" edges (Fig. 4a). As the pH increased to 10.1, the plates become thicker, laminate, and smooth at the edge (Fig. 4b). The lamella stacked by the orientation of plate particles were similar to the results

TABLE II Aqueous pH for pseudoboehmite → bayerite transformation prepared by different starting materials

Starting materials	Transformation pH	Ageing (h)	Ref.
$Al(OH)_3$	7	–	5
$Al(NO_3)_3 \cdot 9H_2O \cdot Zr(NO_3)_2 \cdot 2H_2O$	7.8–8.1	0.5	22
$Al(NO_3)_3 \cdot 9H_2O$ + TEOS	> 9.3	6	This study
$Al(OC_3H_7)_3$ + TEOS	> 10	4	12

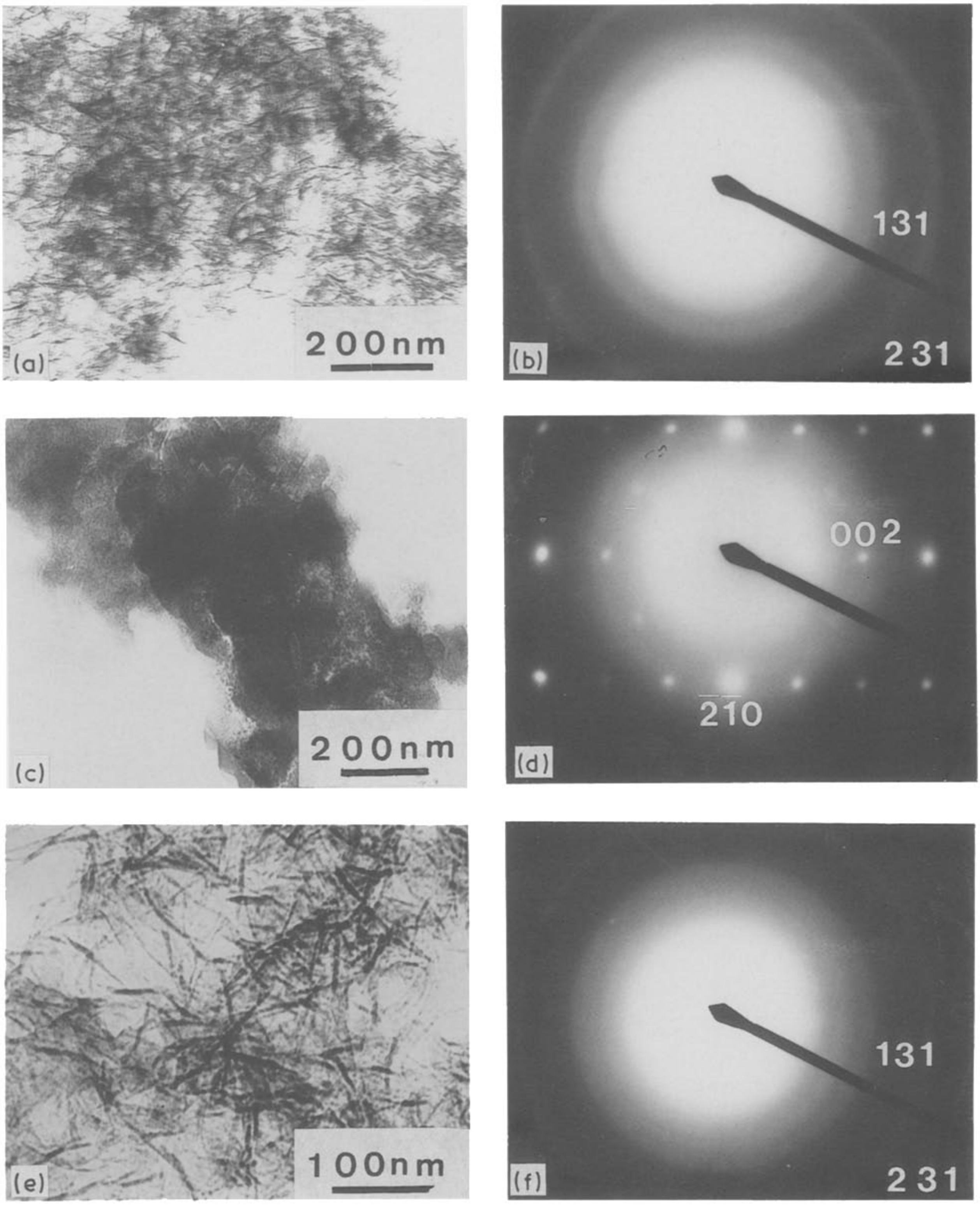

Figure 3 The TEM photographs of particle morphologies of Al_2O_3–SiO_2 xerogels. (a) MA-25 (pH = 8.3, temperature = 25° C), (b) SAD pattern of MA-25. (c) MD-25 (pH = 10.4, temperature 25° C), (d) SAD pattern of MD-25, (e) MB-60 (pH = 9.5, temperature = 60° C), (f) SAD pattern of MB-60.

observed by Sarswati [21]. When the pH reached 10.4, the xerogel was characterized by its drusy surface. The large number of small but loosely accumulated individuals (d = 500 nm) seemed to be hackly fractured (Fig. 4c). The apparent alteration in the morphology of the xerogels resulting from increasing pH values may demonstrate the profound transformation of pseudoboehmite to bayerite in the crystal structure.

The amorphous silicon hydroxide phase could not be found as discrete particle under SEM and TEM observations. It might be absorbed by aluminium hydroxide [22] when gelatinized.

Pseudoboehmite may have a specific surface area of $500\,m^2\,g^{-1}$ [5]. The surface area of xerogel decreased as the pH increased (Fig. 1). It declined from $413\,m^2\,g^{-1}$ at pH = 8.3 to $280\,m^2\,g^{-1}$ at pH = 10.4. A better degree of crystallinity of pseudoboehmite was found at the higher pH values as shown by the X-ray diffractograms. The presence of bayerite at pH > 10.1

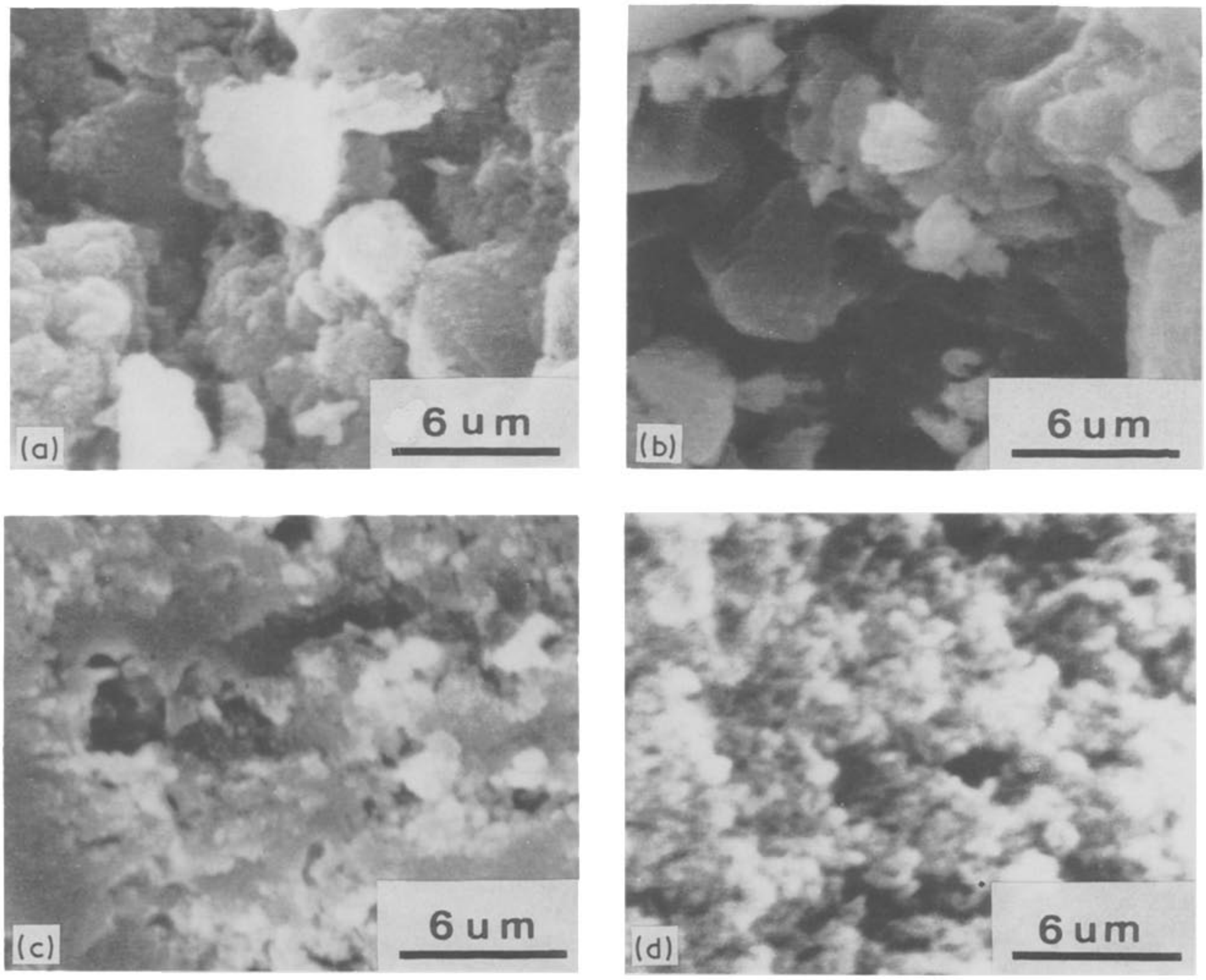

Figure 4 The SEM photographs of morphology of Al_2O_3–SiO_2 xerogels. (a) MA-25, (b) MC-25, (c) MD-25, (d) MB-60.

seemed to depress the observed values of the surface area.

3.2. Effects of $[Al^{3+}]/[Si^{4+}]$

The solubility of $Al(OH)_3$ as a function of pH [23] and the silica adsorption on aluminium hydroxides, which is in relation to the maturity and crystallinity of the aluminium hydroxide gels [22]. As a result the Al_2O_3/SiO_2 contents of the xerogels vary with the pH value of the reaction solution. Fig. 1 which was derived from the solution having $[Al^{3+}]/[Si^{4+}]$ corresponding to stoichiometric mullite demonstrates that the $Al_2O_3/(Al_2O_3 + SiO_2)$ ratios of the precipitates were shifted slightly toward higher pH values when compared with the pure Al_2O_3–H_2O system. Those Al/Si ratios close to stoichiometric mullite can only be formed at a pH value between 9.5 to 10.0.

At fixed pH value, the Al_2O_3 content of the xerogels were highly dependent on the $[Al^{3+}]/[Si^{4+}]$ ratios of the starting solution. For solutions of varying $[Al^{3+}]/[Si^{4+}]$ from 1.8 to 4.8, and at pH = 8.3, higher $[Al^{3+}]$ gave a higher Al_2O_3 content to the xerogels (Table I). Eventually the ratios between aluminium and silicon xerogels were lower than that of the initial solutions. The crystalline phase pseudoboehmite is pH-dependent and not affected by the $[Al^{3+}]/[Si^{4+}]$ of the solution. The value of the surface area of the xerogels displayed a crest at $[Al^{3+}]/[Si^{4+}] = 2.2$ to 3.3 (or $Al_2O_3/(Al_2O_3 + SiO_2) = 0.63$ to 0.72) and seemed not to correspond to the Al_2O_3 contents of the xerogels. The highest value occurred at $[Al^{3+}]/[Si^{4+}] = 3.3$, being $413\,m^2\,g^{-1}$. Increasing or decreasing the $[Al^{3+}]/[Si^{4+}]$ ratios both depressed the values of the surface area. Xerogel of stoichiometric mullite composition was obtained at $[Al^{3+}]/[Si^{4+}] = 3.5$ to 4.3, where the value of specific surface area dropped suddenly from a maximum of $413\,m^2\,g^{-1}$ to $381\,m^2\,g^{-1}$. This value remained constant at the stoichiometric region. The reason for the crestfall was not clear. However, a preliminary investigation of the pseudoboehmite by XRD and TEM techniques revealed that the higher $[Al^{3+}]/[Si^{4+}]$ (at pH = 8.3) environments would favour pseudoboehmite with the crystal growth and its precipitation. A large crystal would breed smaller surface areas.

A variation of the $[Al^{3+}]/[Si^{4+}]$ ratio with constant pH of the starting solution would not alter the features of the colloidal particle.

3.3. Effect of reaction temperature

The effect of the reaction temperature on the formation of the xerogel was examined in two additional samples at 60° C, using the same starting solution at pH near 9.5. It was found that higher reaction temperatures could lower the Al_2O_3 content of the xerogels (Table I). The solubility of silica increases with a rise in temperature [23]. Increasing $[Al^{3+}]$ can decrease the solubility of colloidal and molecular-dispersed silica. The decrease in $Al_2O_3/(Al_2O_3 + SiO_2)$ at higher temperature implies that the redissolution quantities of aluminium hydroxides are greater than that of silicon hydroxides. It did not change the surface area (Table I) of the xerogel which was close to $362\,m^2\,g^{-1}$ and also decreased with an increase in pH.

The pH dependence of the mineral phase of the xerogel seemed to remain. Higher temperatures would not alter the crystalline phase. However, the X-ray diffraction peaks of the high temperature products were more pronounced than those at low temperature (Fig. 2). The growth of the colloidal particles greatly increased with a rise in the reaction temperature. At 60° C (pH 9.5) the pseudoboehmite attained a length of about 150 nm, which is about three times longer than that obtained at 25° C (Fig. 3e). As the surface energy on the individual particles eventually decreased, it caused the nodules to be stacked as dispersed granulars (d = 300 nm) (Fig. 4d).

The growth of pseudoboehmite crystal seems to have no affect on the specific surface area of the xerogel (Fig. 1): the value is $360\,m^2\,g^{-1}$ and may also decrease with an increase in pH. The desorption of silica from pseudoboehmite particles due to pseudoboehmite well crystallization which was also accompanied with an increase in temperature [22] would account for these observations.

4. Conclusion

Properties of the Al_2O_3–SiO_2–H_2O xerogels prepared by aluminium nitrate and TEOS can be explained by two separate systems: Al_2O_3–H_2O [5] and SiO_2–H_2O [4], and are also determined by reaction aqueous conditions. Similar to the Al_2O_3–H_2O system the formation pH was the most important factor controlling the precipitate and crystalline phase in the xerogel. However the values of the pH for the phase transformation of amorphous → boehmite → bayerite are varied and shifted toward higher values due to the preservation of the SiO_2–H_2O system, and the magnitude of the shift may also be affected by homogenous mixing. At present fibrous pseudoboehmite is formed at lower pH (8.3) instead of boehmite. Bayerite is present at pH > 9.5 and eventually becomes predominant at pH > 10.4. Throughout the study the silicon hydroxide of the xerogels was amorphous.

The $[Al^{3+}]/[Si^{4+}]$ ratio obviously affects the Al_2O_3 content of the xerogels, but has less affect on their crystalline phase.

Reaction temperature influence the solubility and the crystallinity of aluminium hydroxide. The pseudoboehmite prepared at 60° C was 150 nm in length, which was about three times that obtained at 25° C in this study.

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References

1. L. M. SPHEPPARD, *Mater. Engng* June (1984) 45.
2. B. B. GHATE, D. P. H. HASSELMAN and R. M. SPRIGGS, *Amer. Ceram. Soc. Bull.* **52** (1973) 670.
3. G.-Y. MENG and R. A. HUGGINS, *Mat. Res. Bull.* **18** (1983) 581.
4. W.-C. WEI, Master Thesis, Case Wetern Reserve Univ. (1984) p. 38.
5. K. WEFERS and G. M. BELL, Alcoa Research Lab., Technical Paper No. 19 (1972).
6. G. C. BYE and K. S. W. SING, in "Particle Growth in Suspension", edited by A. L. Smith (Academic Press, New York, 1972) p. 29.
7. F. W. DYNYS, M. LJUNGBERG and J. W. HALLORAN, in "Better Ceramics Through Chemistry" (Mat. Res. Sc. Sym. Proc. 32, 1984) 321.
8. R. LAMBER, *J. Mater. Sci. Lett.* **5** (1986) 177.
9. W. O. MILLIGAN and H. B. WEISER, *J. Phys. Coll. Chem.* **55** (1951) 490.
10. J. TURKEVICH and J. HILLER, *Anal. Chem.* **21** (1949) 475.
11. Y. HIRATA, H. MINAMIZONO and K. SHIMADA, *Yogyo Kyokai Shi* **93** (1985) 46.
12. D. ALDERFOT and G. C. BYE, *Proc. Brit. Ceram. Soc.* **13** (1969) 125.
13. C.-S. HSI, H.-Y. LU and F.-S. YEN, *J. Amer. Ceram. Soc.* (in preparation).
14. D. W. JOHNSON Jr., *Amer. Ceram. Soc. Bull.* **64** (1985) 1579.
15. E. W. ORRELL and P. J. GIDLEY, *J. Trans. Brit. Ceram. Soc.* **63** (1964) 19.
16. C. J. BRINKER, K. D. KEEFER, D. W. SCHAEFER and C. S. ASHLEY, *J. Non-Cryst. Solids* **48** (1982) 47.
17. J. V. MUYLDER, J. BESSON, W. KUNZ and M. POURBAIX, in "Atlas of Electrochemical Equilibria in Aqueous Solutions" edited by Marcel Pourbaix (NACE, USA, 1974) p. 458.
18. McD. ROBINSON, J. A. PASK and D. W. FUERSTENAU, *J. Amer. Ceram. Soc.* **47** (1964) 516.
19. E. C. MARBOE and S. BENTUR, *Silicates Ind.* **26** (1961) 389.
20. C.-C. CHEN and E.-S. YEN, in "Symposium of Chinese Institute of Mining & Metallurgy Engineering", 1986.
21. V. SARASWATI, G. V. N. RAO and G. V. RAMA RAO, *J. Mater. Sci.* **22** (1987) 2529.
22. I. VALETON, in "Bauxites" (Elsevier Publishing Co., 1972) p. 40.
23. E. DELTOMBE, C. VANLEUGENHAGHE and M. POURBAIX, in "Altas of Electrochemical Equilibria in Aqueous Solutions" edited by Marcel Pourbaix (NACE, USA, 1974) p. 168.

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