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The Thermal Changes in Gels of the SiO_2-Al_2O_3-Sc_2O_3-H_2O System

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The DTA patterns of synthesized coprecipitated gels, the SiO_2–Al_2O_3–Sc_2O_3–H_2O system, resembled that of allophane as well as those of coprecipitated gels, the SiO_2–Al_2O_3–M_2O_3–H_2O system (M: Fe, Ga, or In). The exothermic reaction around 980 °C in the DTA was confirmed to arise from the formation of mullite. The scandium-rich coprecipitated gels showed a new small exothermic peak at about 1000 °C, based on the formation of thortveitite in the DTA. The apparent activation energy for the mullite formation on the coprecipitated gels decreased with an increase in the scandium content. A large portion of the scandium in the coprecipitated gels was deposited as the thortveitite by heating, while that in the mixed gels was deposited as the scandium oxide. The behavior of such trivalent cations as gallium, iron(III), indium, and scandium in the silicoalumina gels was discussed.

In previous papers,[1–3] the properties of amorphous coprecipitated gels in the systems of SiO_2–Al_2O_3–M_2O_3–H_2O (M: Fe, Ga, and In) were found to resemble those of allophane. Scandium ions are considered to replace aluminum ions in the allophane structure, judging from the similarity in their chemical properties. The thermal properties of the gels, the system of SiO_2–Al_2O_3–Sc_2O_3–H_2O, have not been studied, while Toropov *et al.*[4] reported the phase diagram of the Sc_2O_3–Al_2O_3 system. In this paper, the thermal changes in the scandium-bearing coprecipitated gels were studied.

Experimental

Materials. The coprecipitated samples were prepared in the following manner;[1–3] the coprecipitated gels were obtained by boiling mixed solutions of sodium silicate, aluminum sulfate, and scandium sulfate at pH 5.0—5.7, a pH value obtained by adding hexamethylenetetramine; then they were washed by decantation and air-dried for three weeks. The concentration of the scandium ion in the mixed solutions was varied at the constant ratio of 2.0 as $SiO_2/(Al_2O_3+Sc_2O_3)$. All the coprecipitated samples were identified as amorphous from the X-ray powder diffractograms. The scandium-mixed samples were prepared by mixing a synthesized allophane, free from scandium, and an amorphous hydrated scandium oxide in order to compare the properties of the coprecipitated samples. The amorphous hydrate scandium oxide was prepared at pH 5.5 by using hexamethylenetetramine, because the precipitates obtained with ammonia water were identified as crystalline phases of γ-ScOOH[5] or $Sc(OH)_3$.[6]

Procedure. The amounts of SiO_2, Al_2O_3, and $H_2O(\pm)$[7] in the samples were estimated gravimetrically, while that of Sc_2O_3 was estimated by the chelatometry after it has been separated with a cation-exchange resin (Dowex 50W-X8, H-type).[8]

The differential thermal analysis of the samples was carried out in the temperature range from room temperature to 1100 °C at the heating rate of 10 °C/min with a Rigaku Denki Thermoflex, model 8002, differential thermal analyzer.

The X-ray powder diffraction patterns of the samples were taken with an X-ray diffractometer, model JDX-5P, from the Japan Electron Optics Laboratory Co. The samples were heated at 800, 900, 1000, 1100, and 1200 °C for 5 h in order to examine their thermal changes. The relative amounts of the firing-products were identified and estimated by using the diffraction peaks at (120) and (210) of the mullite, those at (110) and (021) of the thortveitite, and that at (222) of the scandium oxide. The unit-cell dimensions of the mullite, one of the firing-products at 1200 °C, were calculated by using the diffraction peaks at (041), (331), and (002) of the mullite. The diffraction angles were calibrated by using those of silicon.

Results

The chemical compositions of the samples are shown in Table 1.

The Differential Thermal Analysis of the Samples. The results of the differential thermal analysis are shown in Fig. 1. Both the coprecipitated and the mixed samples showed a broad endothermic peak and a sharp exothermic peak in the DTA curves at about 100 and 980 °C respectively. The profile of the DTA curves in these samples was similar to that observed in the allophane. The exothermic-peak temperature in the DTA on the coprecipitated gels was scarcely changed in spite of the variation in the scandium content, unlike as in the case of gallium-coprecipitated samples.[2] A new small exothermic peak was observed at about 1000 °C in the coprecipitated samples with more than 7.23 wt% of Sc_2O_3 (the Sc-7C, -8C, and -9C samples).

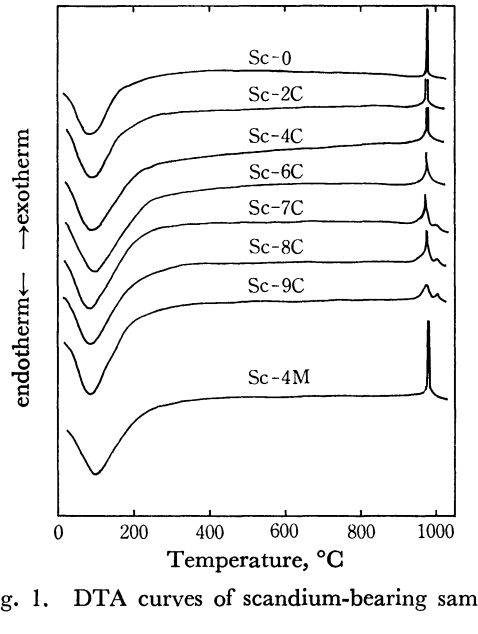

Fig. 1. DTA curves of scandium-bearing samples.

TABLE 1. CHEMICAL COMPOSITIONS OF SCANDIUM-BEARING SAMPLES

Sample	Chemical composition, wt%					Molar ratio	
	SiO_2	Al_2O_3	Sc_2O_3	H_2O (±)	Total	SiO_2/R_2O_3[a)]	H_2O (±)/R_2O_3
Sc-0[b)]	28.01	30.59	—	41.35	99.95	1.55	7.66
Sc-1C[c)]	24.87	32.71	0.40	41.90	99.88	1.28	7.19
Sc-2C	24.15	31.45	1.15	42.49	99.24	1.27	7.45
Sc-3C	22.72	32.75	2.22	42.58	100.27	1.12	7.02
Sc-4C	23.25	30.69	2.77	42.61	99.32	1.21	7.37
Sc-5C	23.43	31.06	3.78	41.86	100.13	1.17	7.00
Sc-6C	25.72	28.39	6.00	40.07	100.18	1.33	6.92
Sc-7C	28.57	25.85	7.23	38.16	99.81	1.55	6.93
Sc-8C	28.04	25.54	8.40	38.43	100.41	1.50	6.86
Sc-9C	26.53	23.87	11.33	38.67	100.40	1.40	6.79
Sc-10M[c)]	27.84	30.41	0.37	41.38	100.0[d)]	1.54	7.64
Sc-11M	27.69	30.24	0.69	41.38	100.0[d)]	1.53	7.62
Sc-12M	27.12	29.61	1.88	41.39	100.0[d)]	1.49	7.57
Sc-13M	26.57	29.02	3.01	41.40	100.0[d)]	1.44	7.51

a) R_2O_3: $Al_2O_3+Sc_2O_3$ b) The sample is the allophane free from scandium. c) The postscript "C" and "M" denote the scandium-coprecipitated and -mixed samples respectively. d) Calculated.

The causes of the exothermic peaks in the DTA were examined as follows: the samples were preheated in the DTA equipment up to temperatures just below and just above their peak temperatures. The phases of the preheated samples were found by X-ray powder diffractometry to be as shown in Table 2. The exothermic reaction at about 980 °C in the coprecipitated samples was found to arise from the formation of mullite, and that at about 1000 °C, from the formation of thortveitite.

The apparent activation energy for the formation of mullite was estimated by means of the method described by Kissinger.[9)] The results for the coprecipitated samples are shown in Table 3.

TABLE 2. PHASES OF PREHEATED SAMPLES

Sample	Peak temp. of original state (°C)	Phase after heat treatment	
		below peak temp. (°C)	above peak temp. (°C)
Sc-0	980	A (975)	M (998)
Sc-2C	982	A (970)	M (987)
Sc-4C	983	A (946)	M (982)
Sc-6C	979	A (967)	M (989)
Sc-8C	981	A (970)	M (993)
	1000		M, T (1010)
Sc-9C	984	A (968)	M (982)
	1000		M, T (1014)
Sc-13M	985	A (962)	M (995)

A; Amorphous, M; Mullite, T; Thortveitite, S; Scandium oxide

TABLE 3. APPARENT ACTIVATION ENERGIES FOR EXOTHERMIC CHANGE AROUND 980 °C

Sample	E_a, kcal/mol
Sc-0	247
Sc-1C	227
Sc-3C	222
Sc-5C	187
Sc-7C	171
Sc-8C	145
Sc-9C	148

The Variation in the Firing-products in the Samples during Heat Treatment. The crystalline phases formed in the heat-treated samples at 800, 900, 1000, 1100, and 1200 °C for 5 h were identified as the mullite, the thortveitite,[10)] and the scandium oxide[11)] by means of X-ray powder diffractometry. The firing-products at each temperatures are shown in Table 4. All the samples formed the mullite above 900 °C, while they were amorphous at 800 °C except for the Sc-12M and -13M samples. The scandium component deposited as the thortveitite in the coprecipitated gels with more than 2.22 wt% of Sc_2O_3, but deposited as the scandium oxide only above 800 °C in the mixed samples. The formation temperature of the thortveitite decreased with an increase in the scandium content. The coprecipitated gel of the SiO_2–Sc_2O_3–H_2O system, with the

TABLE 4. FIRING-PRODUCTS IN THE SAMPLES

Sample	Temperature, °C				
	800	900	1000	1100	1200
Sc-0	A	M	M	M	M
Sc-1C	A	M	M	M	M
Sc-2C	A	M	M	M	M
Sc-3C	A	M	M	M	M,T
Sc-4C	A	M	M	M,T	M,T
Sc-5C	A	M	M	M,T	M,T
Sc-6C	A	M	M	M,T	M,T
Sc-7C	A	M	M,T	M,T	M,T
Sc-8C	A	M	M,T	M,T	M,T
Sc-9C	A	M,T	M,T	M,T	M,T
Sc-10M	A	M	M	M	M
Sc-11M	A	M	M,S	M,S	M,S
Sc-12M	S	M,S	M,S	M,S	M,S
Sc-13M	S	M,S	M,S	M,S	M,S

A; Amorphous, M; Mullite, T; Thortveitite, S; Scandium oxide

SiO_2/Sc_2O_3 molar ratio of 1.79 and free from aluminum, formed the scandium oxide and the thortveitite, while the mixed gels with the same composition formed only the scandium oxide at 1000 °C.

The Unit-cell Dimensions of the Mullite formed in the Heat-treated Samples. The relationships between the unit-cell lengths, a_0, b_0, and c_0, of the mullite formed at 1200 °C for 5 h in the coprecipitated samples and the scadium content in the original samples are shown in Fig. 2. While all the unit-cell lengths increased with an increase in the scandium content up to approximately 4—5 wt%, the increasing tendency in the c_0 was less than those in the a_0 and the b_0. The spacings of the thortveitite formed at 1200 °C were scarcely changed in spite of the variation in the scandium content, while they were slightly smaller than those of a native thortveitite.[10)]

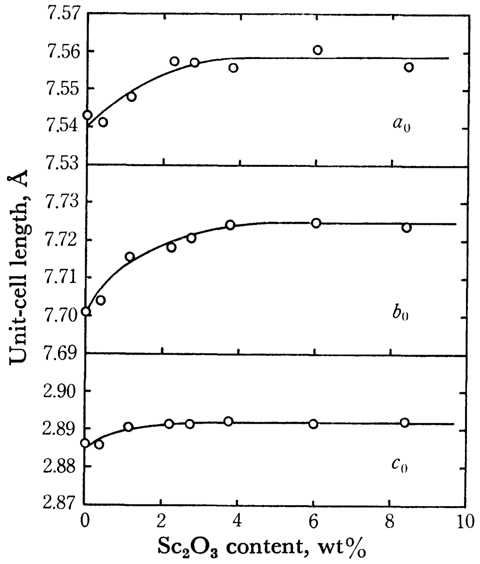

Fig. 2. Relationships between unit-cell length, a_0, b_0, and c_0, of scandium-bearing mullite formed at 1200 °C and Sc_2O_3 content of original gel.

Ďurovič[12)] confirmed that the mullite lattice consisted of a AlO_6 octahedron and AlO_4 and (Si, Al)O_4 tetrahedra, that the AlO_6 octahedra were composed of chains, parallel to the [001] direction, by sharing their edges, and that the chains were linked by the AlO_4 and the (Si, Al)O_4 tetrahedra. Judging from the ratio of the ionic radii of Sc^{3+} and O^{2-} (0.73 and 1.32 Å),[13)] the scandium ions replace the aluminum ions only in the octahedra of the mullite lattice. Variations in the unit-cell lengths, a_0, b_0, and c_0, of the mullite were found to be nonidentical, as is shown in Fig. 2. Because two octahedra slanting to the [100] and the [010] directions are situated in the $\langle 110 \rangle$ directions for each unit-cell of the mullite, though only one octahedron slants in the [001] direction, the replacement of the scandium ions would bring about larger enlargements of the a_0 and the b_0 than that of the c_0. Furthermore, the distortion of the octahedra based on the repulsion between the aluminum ions was considered to decrease slightly by the replacement of the scandium ions, as had also been observed in the octahedra in the α-AlOOH[14)] and the α-ScOOH.[15)] Therefore, the a_0 and b_0 would be further expanded by this effect.

Discussion

A clear difference between the kinds of firing products obtained from the coprecipitated and the mixed gels has been observed in the SiO_2–Al_2O_3–M_2O_3–H_2O systems (M: Fe, Ga, In, and Sc) in this series of works.[1–3)] Judging from these facts, such trivalent cations as iron (III), gallium, indium, and scandium ions were obvious substitutes for the aluminum ions in the allophane structure of the coprecipitated gels. Such trivalent cations were included in the mullite by heating, and they enlarged the lattice; the degree of enlargement is governed by several factors—for example, the amount of the substituting cation, its ionic radius, and the crystallographic geometry, all related to each other.

The order of the amount of trivalent cations includible in the mullite as a solid solution was found to be Ga$\gg$Fe$>$Sc$>$In. This result was considered to be reasonable, judging from the ionic radii of the trivalent cations in these systems (Al^{3+}: 0.51, Ga^{3+}: 0.62, Fe^{3+}: 0.64, Sc^{3+}: 0.73, and In^{3+}: 0.81 Å respectively).[13)]

Léonard *et al.*[16)] have investigated the coordination states of aluminum ions and the structure change in the amorphous hydrated silicoalumina gels by means of X-ray fluorescence spectroscopy and IR spectroscopy. They stated that the aluminum ions were stabilized by forming octahedra sharing corners of the tetrahedra of the SiO_4 and hydroxy-groups in the hydrated silicoalumina gel structure, and that then the sixfold-coordinated aluminum ions were altered to the fourfold-coordinated state as dehydration proceeded upon heating.

The aluminum ion is well known to take both the sixfold- and the fourfold-coordinated states; the gallium ion also can take both the states—for example, in the structure of the β-gallia,[17)] though less frequently than the aluminum ion. The iron (III), however, was not found to form the tetrahedra. The clear difference between the gallium and the iron (III) ions in the degree of substitution was considered to be caused by a variability in the coordination state of the gallium ion in spite of the similarity in their ionic radii.

Though the scandium and the indium ions, having large ionic radii, would replace the aluminum ions to some extent by forming the octahedra in the hydrated silicoalumina gels, the stability of the gels would decrease as a result of the great distortion as dehydration proceeded. The apparent activation energies for the formation of mullite or silicoalumina spinel,[1,2)] a precursor of the mullite, at the coprecipitated gels decreased with an increase in the content of the substituted cations; this decreasing tendency in the scandium- and the indium-coprecipitated samples was larger than that in the gallium-coprecipitated gels. These facts support the above consideration. Though the scandium ions replaced the aluminum ions in the original allophane structure, a large portion of the scandium is probably excluded by heating from the mullite lattice, because the scandium ion took the sixfold-coordinated state only. The deposition of scandium as disilicate in the coprecipitated gels would be caused by its lithophilic nature, and the thortveitite, which has only the sixfold-coordinated sites for metal[18)] in it, is likely to be stable both thermodynamically and crystallographically.

References

1) J. Ossaka, S. Iwai, M. Kasai, T. Shirai, and S. Hamada, This Bulletin, **44**, 716 (1971).

2) M. Kasai, Y. Kudo, and S. Hamada, *ibid.*, **46**, 3091 (1973).

3) M. Kasai, Y. Kudo, and S. Hamada, *ibid.*, **48**, 1608 (1975).

4) N. A. Toropov and V. A. Vail'eva, *Proc. Acad. Sci. USSR*, **152**, 856 (1963).

5) W. O. Milligan and J. L. McAtee, *J. Phys. Chem.*, **60**, 273 (1956).

6) K. Schubert and A. Seitz, *Z. Anorg. Allgem. Chem.*, **256**, 226 (1948).

7) The values were estimated from the ignition loss.

8) H. Hamaguchi, R. Kuroda, K. Aoki, R. Sugishita, and N. Onuma, *Talanta*, **10**, 153 (1963).

9) E. H. Kissinger, *Anal. Chem.*, **29**, 1702 (1957).

10) K. Sakurai, K. Nagashima, and A. Kato, This Bulletin, **35**, 1776 (1962).

11) H. E. Swanson and R. K. Fuyat, NBS Circular 539, Vol. 4, p. 25 (1955).

12) S. Ďurovič, *Chem. Zvesti*, **23**, 113 (1969).

13) "Handbook of Chemistry and Physics," ed. by R. C. Weast, CRC Press, Cleveland (1974), p. F-194.

14) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **11**, 798 (1958).

15) A. N. Christensen and S. J. Jensen, *Acta Chem. Scand.*, **21**, 121 (1967).

16) A. Léonard, S. Suzuki, J. J. Fripat, and C. De Kimpe, *J. Phys. Chem.*, **68**, 2608 (1964).

17) S. Geller, *J. Chem. Phys.*, **33**, 676 (1960).

18) "Comprehensive Inorganic Chemistry," Vol. 3, ed. by J. C. Bailar *et al.*, Pergamon Press, Oxford (1973), p. 332.