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STRUCTURAL ORGANIZATION IN AMORPHOUS SILICO-ALUMINAS

P. CLOOS*, A. J. LÉONARD*, J. P. MOREAU†, A. HERBILLON‡ and J. J. FRIPIAT‡

Laboratoire de Physico-Chimie Minérale, Institut des Sciences de la Terre, 42, de Croylaan, Heverlee-Louvain, Belgium

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Abstract—A structure model for amorphous hydrated or dehydrated silico-aluminas with composition varying between $0 < Al:Al+Si < 1$ is presented. A central core made from a tetrahedral network in which silicon is partially substituted by aluminium carries a net negative electrical charge. This charge is balanced by more or less polymerized hydroxyaluminium cations forming a coating around the core.

As $Al:Al+Si$ increases, the number of substitutions in the core increases as well as the complexity of the hydroxyaluminium cations in the coating.

For $Al:Al+Si \geq 0{\cdot}8$, a demixing is observed, leading to the formation of a crystalline pseudo-boehmite and bayerite.

Upon heating, the coating as well as the demixed phases are transformed into a spinel structure containing tetrahedral aluminium, while the core structure remains unaffected.

This model could explain the solubility features, the phosphate reaction and the catalytic properties of amorphous silico-aluminas.

INTRODUCTION

SYNTHETIC silico-aluminas, characterized by large specific surface areas and high surface acidity, are commonly used as cracking catalysts. The acidity and catalytic activity of these compounds are generally attributed to the presence of structure defects, the nature of which has not yet been precisely defined.

Moreover, the colloidal fraction of many soils contains large quantities of amorphous material with various $Al_2O_3/SiO_2 + Al_2O_3$ compositions. In soils derived from volcanic ashes, these amorphous clay minerals are commonly called "allophanes". It is believed that coprecipitation of silica and alumina is one of the dominant processes of their formation, which according to Kanno *et al.*(1968) proceeds through desilication and hydration of glasses in pumices and ashes and replacement of Si–O–Si linkages by Si–O–Al bonds. More generally, allophane is known to be produced by weathering of volcanic ash, basic and ultra-basic rocks, by the grinding of minerals, and by the podzolising process (Furkert and Fieldes, 1968). However, the genetic links suggested by the natural association of allophane with clay minerals like metahalloysite, kaolinite, chlorites, intergrades, and gibbsite, etc., do not always appear quite clearly (Egawa, 1964; Wada and Matsubara, 1968).

The amorphous character of these compounds seems to be responsible for their peculiar properties, i.e. their high adsorption power for water, organic matter and phosphates, and the low degree of availability of adsorbed phosphorus.

STRUCTURE REVIEW

In the numerous contributions dealing with the structure of amorphous silico-aluminas, emphasis is laid on the type of aluminium bonding.

In order to explain the acidity and catalytic activity of such compounds, Thomas (1949) suggests that the catalyst is not merely a mixture of silica and alumina, but a real chemical combination of both elements. Assuming that a positive hydrogen ion is associated with tetrahedral aluminium, and that the catalytic activity is due to this acidic hydrogen, the active constituent might be written as $(HAlSiO_4)_x$.

In many preparative procedures for cracking catalysts, a silica hydrogel is first prepared. The formation of acid sites is explained by the condensation of the surface hydroxyl groups of the incompletely polymerized silica hydrogel with the hydroxyl groups of the hydrolyzed aluminium ions (Tamele, 1950). Milliken *et al.* (1950) and Oblad *et al.* (1951) consider that silico-aluminas are made up of silica and alumina particles, interbonded by the condensation of the hydroxyls at their interfaces. The silica tetrahedral structure will induce the local formation of fourfold coordinated alum-

*The University of Louvain.
†Research Associated to "Ciments Lafarge", France.
‡The University of Louvain and M.R.A.C. (Tervuren).

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inium giving rise to an aluminate-like structure. Bases and/or strongly electropositive cations act as stabilizing and stimulating agents for this aluminate-like arrangement. Above a critical alumina content (15–30 per cent), the amount of aluminate decreases steadily with the decreasing percentage of silica. The excess of alumina in the silico-alumina mixture crystallizes into boehmite and hydrargillite.

According to Danforth (1960), aluminium is present under three forms: free alumina, aluminium bound to silica and aluminium hydroxide neutralizing acid exchange sites. In opposition to Milliken *et al.* (1950), this author considers that an alumina tetrahedron sharing corners with silica tetrahedra acts as Brönsted acid. The alumina linked by two or three bonds to silica would form Lewis acids on dehydration.

According to the pretreatment temperature and to the aluminium content, Léonard *et al.* (1964) distinguish three oxygen environments for the aluminium atoms (1) alumina octahedra and (2) alumina tetrahedra sharing corners, or (3) edges. In these structures, Fripiat *et al.* (1965) characterize two probable types of acid sites: (1) in the dehydrated samples, Lewis sites located on silicon and aluminium atoms according to whether the compounds are rich or poor in aluminium and (2) in the hydrated samples and regardless of the composition, Brönsted sites originating from isomorphic substitutions of silicon by aluminium in the tetrahedral silica network.

For allophanes the problem of structure determination is still more complex than for catalysts, because of their pollution by hydrated iron oxides, organic matter and crystalline clay minerals, which are difficult, if not impossible, to remove selectively without damaging the allophane. Fieldes (1955) has identified two forms of allophane. In variety A, very small colloidal particles of hydrous alumina are considered to be randomly cross-linked by silica tetrahedra, whereas B would consist in a mixture of discrete hydrous oxides of aluminium and silicon.

Both kinds of allophanes are essentially amorphous, but they may be characterized by D.T.A.: A shows a high temperature exothermic reaction, whilst B does not (Furkert and Fieldes, 1968). The formation of allophane A from volcanic ash has been shown (Fieldes, 1966) to be due to structural randomness in volcanic glass and imperfect structures in component felspars.

STRUCTURAL MODEL

In this paper a schematic structural model for amorphous silico-aluminas is presented, as shown in Fig. 1: it could stand, as a first approximation, for silico-alumina catalysts as well as for allophane. The basic assumption in this model is that silico-alumina gels are made from a core in which tetrahedral silicon is partially substituted by aluminium and from an alumina coating surrounding the core. The negative charge in the core is compensated, at least partially, by the positive charge of mono- or polymeric hydroxyaluminium cations ($Al(OH)_2^+$ or $Al_n(OH)_m^{(3n-m)+}$) in the coating. On increasing the Al: Al + Si ratio, the complexity of these polymeric cations increases, whilst the net charge per aluminium atom decreases. At very high Al: Al + Si ratios ($> 0{\cdot}8$), this charge tends to zero and a demixing is observed; i.e. a third phase composed of pseudo-boehmite and bayerite appears (Fig. 2).

A similar model was suggested independently by de Villiers and Jackson (1967) and by Cloos *et al.* (1968).

The deductions of the first authors are based on cation exchange properties of aluminized clay and the equivalent properties observed for allophane, whereas the model proposed by Cloos *et al.* (1968), working with synthetic silico-aluminas, proceeds mainly from the following criteria:

(1) The only charge balancing cations in the system are protons due to hydrolysis and aluminium ions, since the samples are prepared by slow hydrolysis of aluminium isopropoxide and ethyl silicate in plastic beakers (Léonard *et al.*, 1964).

(2) The cation exchange capacity (C.E.C.) values, determined by ammonium acetate at pH 7, are lower than the potential C.E.C. values computed from the fourfold coordinated aluminium content, obtained by using the X-ray fluorescence technique (White *et al.*, 1958; De Kimpe *et al.*, 1961, 1964; Gastuche *et al.*, 1962, 1963; Léonard *et al.*, 1964). The observed discrepancy is particularly high in the composition range $0{\cdot}40 \leqslant Al:Al+Si \leqslant 1{\cdot}0$, where the sixfold coordinated aluminium content increases rapidly. This discrepancy between the experimental and theoretical C.E.C. was interpreted as an indication that the exchange sites of the silico-alumina particles might be balanced, at least to some extent, by a more or less complex form of hydroxyaluminium cations, like those suggested by Jackson (1960), Hsu and Rich (1960), Cashen (1963, 1966), Brosset *et al.* (1964), Hsu and Bates (1964) and Fripiat *et al.* (1965). The increasing complexity of these hydroxyaluminium cations with increasing Al: Al + Si ratios and increasing precipitation pH (4–7) prevents the exchange by a monovalent cation at pH 7.

(3) The amounts of aluminium released at pH above 3 (Table 1) is inversely correlated to the aluminium content of the samples.

The apparent aluminium coordination number measurements suggested that practically all the

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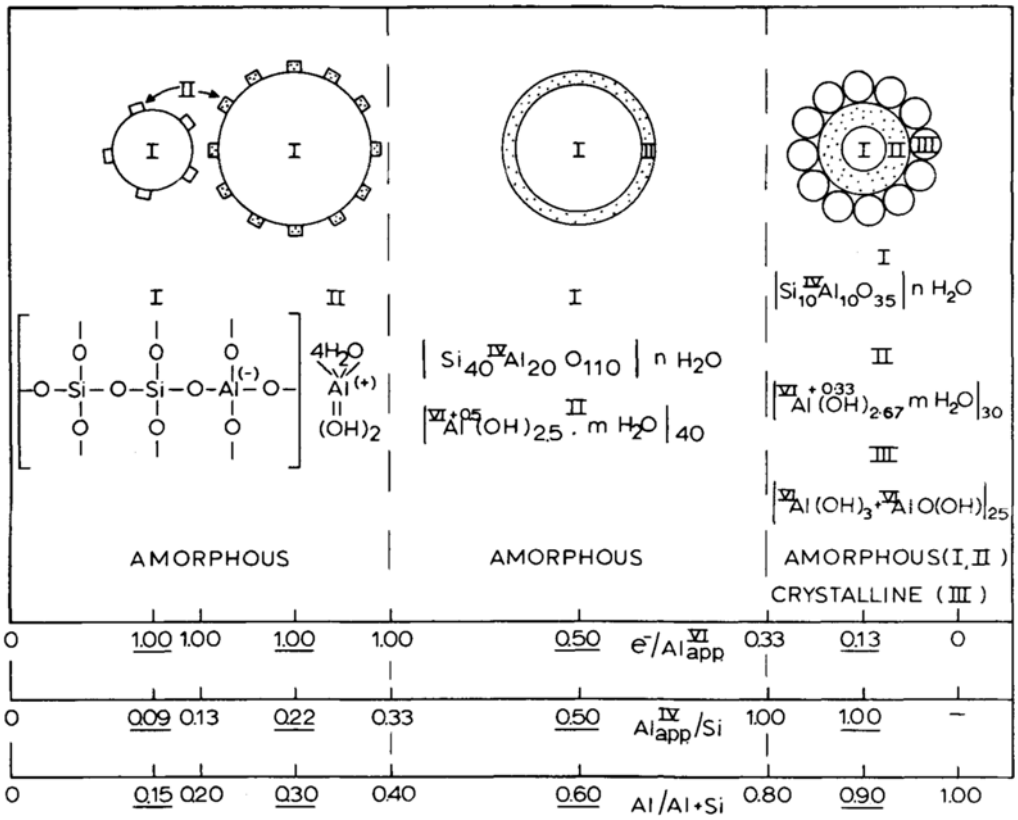


Fig. 1. Schematic representation and structural formulas of silico-aluminas with varying Al: Al + Si ratios. I – Amorphous silico-alumina core; II – Amorphous alumina coating; III – Crystalline aluminas. The models correspond to the specified figures in abscissa.

Table 1. Release of soluble aluminium at different pH values*

pH	Reagent	Method	Aluminium (m-equiv./100 g) released from the following composition (Al/Al + Si)		
			0·3	0·53	0·85
7	KCl N	3 consecutive washings of 100 mg solid with a 10 ml solution	13·7	9·9	1·0
4·5	KCl N acidfied with HCl	idem	24·2	16·7	4·0

*Cloos *et al.* (1968).

aluminium cations in the core are tetrahedrally coordinated in the range $0 < Al : Al + Si \leqslant 0{\cdot}4$ and that, surprisingly enough, for $Al : Al + Si \geqslant 0{\cdot}8$, the $Al^{IV}_{app.}$: Si ratio in the silico-alumina particle was higher than one.

The original model of Cloos *et al.* (1968) has been reexamined in the light of new experimental data (Table 2).

These new considerations proceed from the choice of different standards for the determination of apparent aluminium coordination numbers and from results obtained from generalized Fourier

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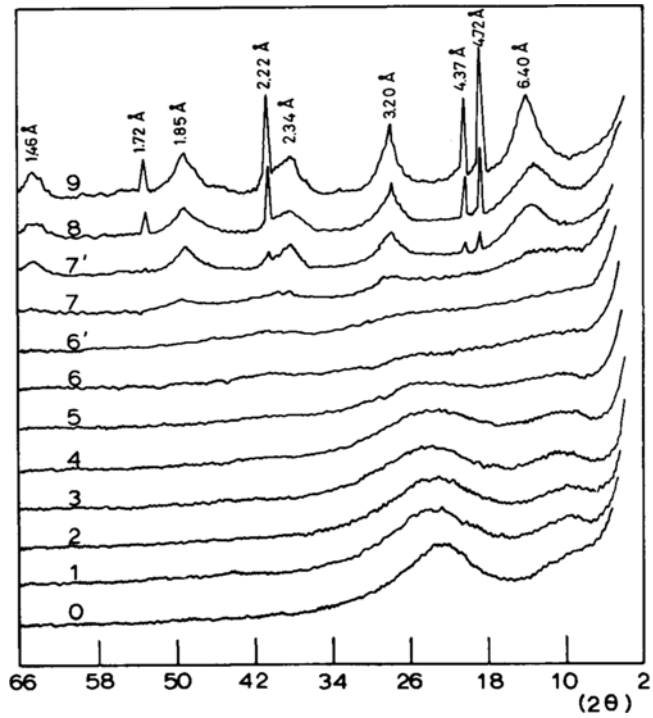


Fig. 2. X-ray diffraction patterns (CuKα radiation) of silico-aluminas with varying Al: Al + Si ratios. 0–9: samples of Table 2; 6′ sample of composition Al: Al + Si = 0·75 (De Kimpe, 1967); 7′ sample of composition Al: Al + Si = 0·85 (Cloos *et al.*, 1968). Reflexions at 6·40, 3·20, 2·34, 1·85 and 1·46 Å: pseudoboehmite; reflexions at 4·72, 4·37, 3·20, 2·22 and 1·72 Å: bayerite.

Table 2. Chemical composition, cation exchange capacity (C.E.C.), specific surface area (So), and apparent contents in fourfold coordinated aluminium of silico-aluminas dried at 100°C

Samples	Ignition loss (%)	SiO_2 (%)	Al_2O_3 (%)	$\frac{Al}{Al+Si}$	C.E.C. (m-equiv./100 g)	So (m^2/g)	$\frac{Al^{IV}_{app}}{Al+Si}$
0	7·28	92·72	0	0	9·6	939	0
1	10·81	74·91	13·23	0·167	139·5	470	0·101
2	12·49	68·35	17·76	0·228	136·6	309	0·120
3	14·65	61·64	24·57	0·311	133·4	230	0·161
4	16·56	48·95	32·72	0·431	112·6	198	0·200
5	19·73	34·62	44·33	0·592	80·0	275	0·220
6	21·63	26·24	50·16	0·685	57·0	303	0·195
7	21·33	14·00	61·38	0·833	22·5	405	0·185
8	20·59	5·92	78·96	0·938	9·6	314	0·023
9	24·56	0	75·44	1·000	1·3	215	0

analysis (radial distribution). In a first paper (Léonard *et al.*, 1964), calcined $AlPO_4$ and kaolinite were used as standards for Al^{IV} and Al^{VI} respectively. It was shown later (Léonard *et al.*, 1967*a*) that in amorphous hydrated and transition aluminas, the aluminium coordination numbers derived from Fourier analysis agree fairly well with those obtained by X-ray fluorescence technique, when Na-zeolite and gibbsite are used as standards for Al^{IV} and Al^{VI} respectively. However for crystalline

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transition aluminas (Léonard *et al.*, 1967*b*), the $Al^{IV}_{app.}$ contents determined by X-ray fluorescence were found in disagreement with the Fourier analysis results, the discrepancy for a given phase being more pronounced as the pretreatment temperature is increased (Fig. 3). It was shown that this discrepancy is due to changes in the Al–O average bond lengths within a constant Al^{IV} content. $0{\cdot}4 \leqslant Al:Al+Si \leqslant 0{\cdot}8$. For the sake of simplification, this assumption will be adopted.

As, in the same range, the Si content decreases, the $Al^{IV}_{app.}$: Si ratio increases (see Fig. 1) and reaches a maximum value of 1·0 for $Al:Al+Si \simeq 0{\cdot}8$. Above this limit the $Al^{IV}_{app.}$: Si ratio remains constant, and simultaneously a new crystalline phase demixes (Fig. 2). The calculations of the structural

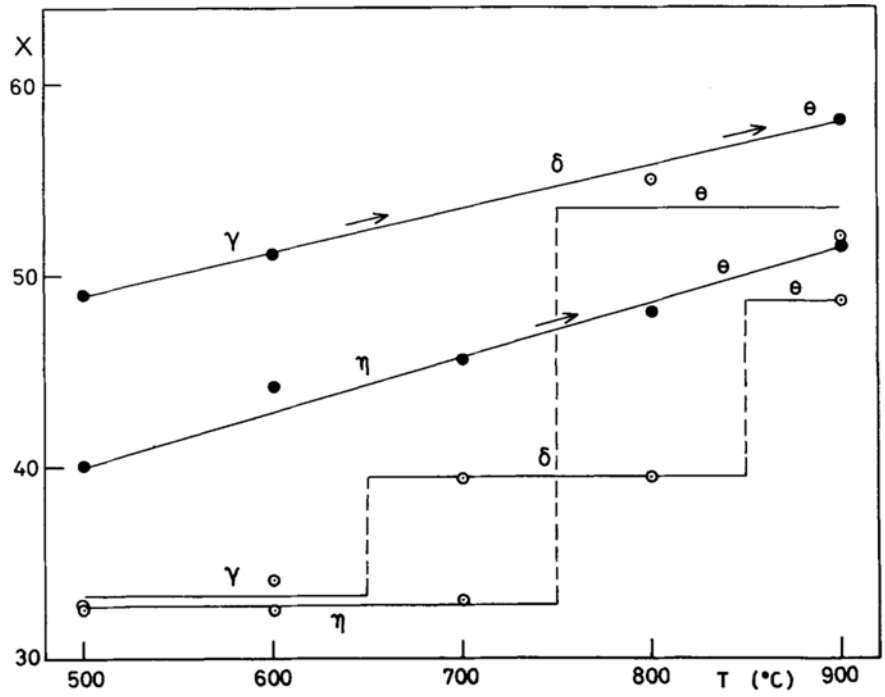


Fig. 3. Variation of the Al^{IV} content X (per cent) in crystalline transition aluminas obtained from X-ray fluorescence ($Al^{IV}_{app.}$●) and from diffuse X-ray scattering ⊙ measurements as a function of pretreatment temperature.

In Fig. 4 the X-ray fluorescence $Al^{IV}_{app.}$ contents, obtained by using zeolite and gibbsite standards, are plotted as a function of composition. The experimental points refer to the samples of Table 2 and to those described by Léonard *et al.*, (1964).

Let us first consider the samples dried at low temperature (100 or 200°C). In the composition range $0 < Al:Al+Si \leqslant 0{\cdot}4$, about 50 per cent of the total aluminium content appears as fourfold coordinated and is assumed to be in the core.

As the total aluminium content is increased, the relative $Al^{IV}_{app.}$ content decreases, and, obviously, the experimental data are more scattered than in the first range. This may be due, to some extent, to slight differences in the preparation techniques (stirring, ageing, drying, etc.). The best fitting line should be approximately horizontal in the range formulas, represented in Fig. 1, are based on these considerations.

The composition of the alumina coating distributed around the core is obtained in the following manner. The total charge of the polymeric complex is assumed to be equal to the number of Al/Si substitution in the core. In these complexes, aluminium is of course octahedrally coordinated. The composition is obtained by difference between the total aluminium content and the core composition.

As according to this model, the $Al^{IV}_{app.}$: Si ratio in the silico-alumina core increases continuously up to a value of one in the range $0 < Al:Al+Si < 0{\cdot}8$, it may be assumed that the corresponding structures will become more and more fragile. This has been actually confirmed by a kinetic study of acid

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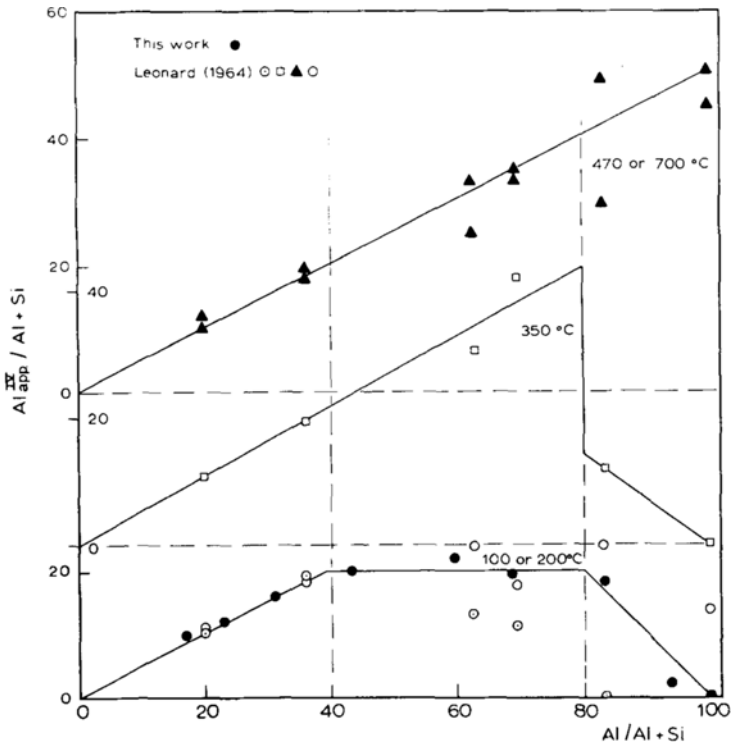


Fig. 4. Apparent ($Al^{IV}_{app.}$) content ($Al^{IV}_{app.}$/Al + Si per cent) as a function of composition (Al/Al + Si, per cent) and of pretreatment temperature.

dissolution at 25°C (Table 3). As this attack is mainly ruled by two factors, i.e. accessibility to the reagent, related to the specific surface area, and fragility related to the $Al^{IV}_{app.}$: Si ratio, the data of Table 3 may be interpreted as a valid evidence for the above hypothesis.

Considering now the heated samples (350°, 470° and 700°C), it is seen (Fig. 4) that in the range $0 < Al : Al + Si \leqslant 0{\cdot}4$ the $Al^{IV}_{app.} : Al^{VI}_{app.}$ ratio is not at all affected by the heat treatment. On the contrary, for samples in the composition range $0{\cdot}4 < Al : Al + Si \leqslant 0{\cdot}8$, the heat treatment induces a similar increase in the $Al^{IV}_{app.}$ content, this increase being the largest for the largest total Al content.

In the composition range $0{\cdot}8 \leqslant Al : Al + Si \leqslant 1{\cdot}0$, where crystalline alumina is present, heating at 350°C does not modify the original $Al^{IV}_{app.}$ contents, whereas at 470 and 700°C, a similar evolution as that in the preceding range is observed.

It must be emphasized here, that these data in connection with those of Fig. 3, do not permit the computation of the real Al^{IV} content. They may only be interpreted as an indication that Al^{VI} is differently affected by heat treatment according to whether it belongs to isolated hydroxyaluminium cations, to high polymeric species, or to crystalline alumina.

By comparison with data obtained for transition aluminas, it may be concluded that a spinel phase is formed in the alumina coating to an extent depending on its polymerization state and on the temperature. On the contrary, the core structure should roughly be temperature independent.

Table 3. Kinetic data of $Al^{IV}_{app.}$ extraction at 25°C by 0·2 N HCl at constant (m-equiv. H^+/m-equiv. Al = 20) ratio in correlation with the specific surface area and the $Al^{IV}_{app.}$/Si composition

Samples	$Al^{IV}_{app.}$ extraction (%/hr)	So (m^2/g)	$Al^{IV}_{app.}$/Si
1	0·75	470	0·122
2	1·22	309	0·155
3	0·87	230	0·236
4	1·72	198	0·352
5	21·24	275	0·540
6	100·00	303	0·620

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CONCLUSIONS

The schematic structural model proposed here is certainly not perfect. Nevertheless it presents the advantage of offering a possible explanation for a number of experimental observations.

(1) It has been suggested (Takahashi, 1964, and Saunders, 1965) that in soils containing allophane, the Al: Al + Si ratio is the determining factor for phosphate adsorption and availability, the former increasing and the latter decreasing with increasing aluminium content in the amorphous phase. Assuming that hydroxyaluminium cations, saturating the negative charge of the silico-alumina core, play an important role in the phosphate adsorption processes, the behaviour of allophane with this respect is easily understood. The higher the Al: Al + Si ratio, the higher the concentration of surface alumina and the higher the fixation level of phosphate. As the increase in the Al content implies an increasing complexity, and hence a decreasing solubility of the hydroxyaluminium polymers, phosphate availability decreases accordingly.

(2) The genesis of crystalline aluminium hydroxides and phyllites from amorphous silico-aluminas may be considered in relation with the proposed model.

A parallel may be drawn between the "antigibbsitic effect" (Jackson, 1963) described for vermiculite and montmorillonite containing polymeric hydroxyaluminium cations in their interlamellar space, and the observation made here, that crystalline aluminium hydroxide demixes only at very high aluminium contents. For intergrades described by Jackson (1963), the "antigibbsitic effect" is well marked up to an Al: Al + Si ratio of about 0·6 (corresponding approximately to a 2:2 structure), whereas in the amorphous silico-aluminas studied here, the crystalline phase appears only for a composition Al: Al + Si $\geq$ 0·8. This enhancement of the "antigibbsitic effect" in amorphous silico-aluminas may be attributed to the higher surface density of charge of the silico-alumina core, and to its unability to nucleate on its surface the gibbsite-like lattice.

Poncelet and Brindley (1967) report that the Al-montmorillonite intergrade is transformed at 175°C into kaolinite, whereas De Kimpe (1967) observes that a silico-alumina of the same composition demixes into boehmite and into a silico-alumina core with a higher silicon content.

(3) In the domain of catalysis, it is known that silico-aluminas in the composition range of Al: Al + Si $<$ 0·3 have a different behaviour than those richer in aluminium. As soon as the polymerization degree of hydroxyaluminium cations in the coating becomes high enough, the behaviour of the calcined sample becomes more similar to that of transition aluminas. This is in agreement with the structure proposed here for the alumina coating in the high Al: Al + Si range. In the low Al: Al + Si terms, the core surface is not saturated by a complex hydroxyaluminium cation but by more or less isolated species with a higher positive charge per aluminium atom. Barthomeuf *et al.*, (1967) have shown that 80 per cent of the aluminium contents of a cracking catalyst with a composition $Al_2O_3/Al_2O_3 + SiO_2 = 0{\cdot}13$ may be removed by acid leaching without affecting the catalytic activity.

This could be explained assuming that sixfold coordinated aluminium on the core surface is removed firstly, leaving an almost intact internal structure.

In conclusion, it is the authors' hope that the suggested model will stimulate further works and discussions.

REFERENCES

Barthomeuf, D., Ballivet, D., Devaux, R., and Trambouze, Y. (1967) Caractérisation de la phase active dans un catalyseur silice-alumine: *Bull. Soc. Chim. France* 1495–1502.

Brosset, C., Biedermann, G., and Sillen, L. G. (1954) Studies on the hydrolysis of metal ions: *Acta Chem. Scand.* **8**, 1917–1926.

Cashen, G. H. (1963) Electric charges and thixotropy of clays: *Nature* **197**, 349–350.

Cashen, G. H. (1966) Electric charges of clays: *J. Soil Sci.* **17**, 303–315.

Cloos, P., Herbillon, A., and Echeverria, J. (1968) Allophane-like synthetic silico-aluminas. Phosphate adsorption and availability: *Trans 9th Intern. Congr. Soil Sci.* **II**, 733–743.

Danforth, J. D. (1960) Structures and chemical characteristics of cracking catalysts by ion exchange: *Actes 2e Congr. Intern. Catalyse, Paris* **1**, 1271–1286.

De Kimpe, C., Gastuche, M. C., and Brindley, G. W. (1961) Ionic coordination in alumino-silicic gels in relation to clay mineral formation: *Am. Mineralogist* **46**, 1370–1381.

De Kimpe, C., Gastuche, M. C., and Brindley, G. W. (1964) Low temperature syntheses of kaolin minerals: *Am. Mineralogist* **49**, 1–16.

De Kimpe, (1967) C. Hydrothermal aging of synthetic alumino-silicate gels: *Clay Minerals* **7**, 203–214.

de Villiers, J. M., and Jackson, M. L. (1967) Cation exchange capacity variations with pH in soil clays: *Soil Sci. Soc. Am. Proc.* **31**, 473–476.

Egawa, T. (1964) Volcanic Ash Soils in Japan: Ministry of Agriculture and Forestry, Japanese Govt., Chap. 3, p. 27.

Fieldes, M. (1955) Clay mineralogy of New Zealand soils: Part II. Allophane and related mineral colloids: *New Zealand J. Sci. Technol.* **37B**, 336–350.

Fieldes, M. (1966) The nature of allophane in soils—I. Significance of structural randomness in pedogenesis: *New Zealand J. Sci.* **9**, 599–607.

https://doi.org/10.1346/CCMN.1969.0170505 Published online by Cambridge University Press

Fripiat, J. J., Van Cauwelaert, F., and Bosmans, H. (1965) Structure of aluminum cations in aqueous solutions: *J. Phys. Chem.* **69**, 2458–2462.

Fripiat, J. J., Léonard, A., and Uytterhoeven, J. B. (1965) Structure and properties of amorphous silicoaluminas – II. Lewis and Brønsted acid sites: *J. Phys. Chem.* **69**, 3274–3279.

Furkert, R. J., and Fieldes, M. (1968) Allophane in New Zealand soils: *Trans 9th Intern. Congr. Soil Sci.* **III**, 133–141.

Gastuche, Marie-Claire, and Herbillon, Adrien (1962) Etude des gels d'alumine: cristallisation en milieu désionisé: *Bull. Soc. Chim. France* 1404–1412.

Gastuche, M. C., Toussaint, F., Fripiat, J. J. Touillaux, R., and Van Meerssche, M. (1963) Study of intermediate stages in the kaolin–metakaolin transformation: *Clay Min. Bull.* **5**, 227–236.

Hsu, P. H., and Rich, C. I. (1960) Aluminum fixation in a synthetic cation exchanger: *Soil Sci. Soc. Am. Proc.* **24**, 21–25.

Hsu, P. H., and Bates, T. F. (1964) Formation of X-ray amorphous and crystalline aluminium hydroxides: *Mineral. Mag.* **33**, 749–768.

Jackson, M. L. (1960) Structural role of hydronium in layer silicates during soil genesis: *Trans 7th Intern. Congr. Soil Sci.* **2**, 445–455.

Jackson, M. L. (1963) Interlayering of expansible layer silicates in soils by chemical weathering: *Clays and Clay Minerals* **11**, 29–46.

Kanno, I., Onikura, Y., and Higashi, T. (1968) Weathering and clay mineralogical characteristics of volcanic ashes and pumices in Japan: *Trans 9th Intern. Congr. Soil Sci.* **III**, 111–122.

Léonard, A., Suzuki, Sho, Fripiat, J. J., and De Kimpe, C. (1964) Structure and properties of amorphous silicoaluminas – I. Structure from X-ray fluorescence spectroscopy and i.r. spectroscopy: *J. Phys. Chem.* **68**, 2608–2617.

Léonard, A. J., Van Cauwelaert, F., and Fripiat, J. J. (1967*a*) Structure and properties of amorphous silicoaluminas – III. Hydrated aluminas and transition aluminas: *J. Phys. Chem.* **71**, 695–708.

Léonard, A. J., Semaille, P. N., and Fripiat, J. J. (1967*b*): *Proc. Brit. Ceram. Soc., London*, In press.

Milliken, T., Mills, G. A., and Oblad, A. G. (1950) The chemical characteristics and structure of cracking catalysts: *Discussions Faraday Soc.* **8**, 279–290.

Oblad, A. G., Milliken, T. H., Jr., and Mills, G. A. (1951) Chemical characteristics and structure of cracking catalysts: *Advan. Catalysis* **III**, 199–247.

Oblad, A. G., Milliken, T. H., and Mills, G. A. (1951): *Rev. Inst. Franç. Pétrole Ann. Combust. Liquides* **6**, 343.

Poncelet, G. M., and Brindley, G. W. (1967) Experimental formation of kaolinite from montmorillonite at low temperatures: *Am. Mineralogist* **52**, 1161–1173.

Saunders, W. M. H., (1965) Phosphate retention by New Zealand soils and its relationship to free sesquioxides, organic matter, and other soil properties: *New Zealand J. Agr. Res.* **8**, 30–57.

Takahashi, T. (1964) Aluminium in volcanic-ash soils. Changes in physico-chemical properties of soils by cultivation: Kyushu Nogyo, Shikensho Tho **10**, 205–246.

Tamele, M. W. (1950) Chemistry of the surface and the activity of alumina-silica cracking catalysts: *Discussions Faraday Soc.* **8**, 270–279.

Thomas, Charles L. (1949) Chemistry of cracking catalysts: *Ind. Eng. Chem.* **41**, 2564–2573.

Wada, K., and Matsubara, I. (1968) Differential formation of allophane, "Imogolite" and gibbsite in the Kitakami pumice bed: *Trans 9th Intern. Congr. Soil Sci.* **III**, 123–131.

White, E., McKinstry, H., and Bates, T. F. (1958) Crystal chemical studies by X-ray fluorescence: *7th Ann. Conf. X-ray Anal., Denver* **2**, 239–245.

Résumé – In modèle présente de structure pour des silico-alumines amorphes hydratés ou deshydratés, dont la composition varie entre $O < Al:Al+Si < 1$. Un noyau central construit à partir d'un réseau tetraédrique dans lequel la silice est substituée en partie par l'aluminium, porte une charge électrique négative. Cette charge est équilibrée par des cations hydroxy-aluminium plus ou moins polymérisés formant une couche autour du noyau. Tandis que $Al:Al+Si$ augmentent, le nombre de substitutions dans le noyau s'accroit ainsi que la complexité des cations hydroxy-aluminium dans le revêtement. Pour $Al:Al+Si \geqslant 0{,}8$, on observe un démixage qui conduit à la formation d'un pseudo-boehmite cristallin et bayerite. Par l'action du chauffage, le revêtement ainsi que les phases de démixage sont transformés en une structure spinelle contenant de l'aluminium tétrahydrique, tandis que la structure du noyau rest inchangée. Ce modèle pourrait expliquer les caractéristiques de solubilité, la réaction du phosphate et les propriétés catalytiques des silico-alumines amorphes.

Kurzreferat – Ein Strukturmodell für amorphe hydrierte bzw. dehydrierte Silica-Tonerden mit einer Zusammensetzung zwischen $O < Al:Al+Si < 1$ wird erörtert. Ein zentraler Kern, der aus einem tetrahedralen Netz, in dem Silizium teilweise durch Aluminium substituiert ist, besteht, trägt eine Nettoladung negativer Elektrizität. Diese Ladung wird durch mehr oder weniger polymerisierte Hydroxy-Aluminium-Kationen ausgeglichen, die eine Schale rings um den Kern bilden. Mit zunehmenden $Al:Al+Si$ nimmt auch die Anzahl der Substituierungen in dem Kern zu, wie auch die Kompliziertheit der Hydroxy-Aluminium-Kationen in der Schale. Bei $Al:Al+Si \geqslant 0{,}8$ beobachtet man eine Entmischung, die zur Bildung von kristallischem Pseudoböhmit und Bayerit führt. Nach der Erwärmung werden die Schale und die entmischten Phasen in eine Spinellstruktur umgewandelt, die tetrahedrales Aluminium enthält, während die Kernstruktur unberührt bleibt. Dieses Modell könnte die Löslichkeitsmerkmale, die Phosphatreaktion und die katalytischen Eigenschaften amorphe-Silica-Tonerden erklären.

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Резюме—Предложена структурная модель для аморфной гидратированной или дегидратированной смеси кремнезема и глинозема, состав которой изменяется в пределах: $O < Al : Al + Si < 1$. Внутреннее ядро образовано тетраэдрической сеткой, в которой кремний частью замещен алюминием; сетка имеет отрицательный заряд. Этот заряд компенсируется более или менее полимеризованными гидроксиалюминиевыми катионами, образующими оболочку вокруг ядра.

С возрастанием отношения $Al: Al + Si$ число замещений в ядре увеличивается, а комплексность гидроксиалюминиевых катионов в оболочках усиливается.

При отношении $Al: Al + Si \geqslant 0{,}8$ наблюдалось обособление глинозема с образованием кристаллических псевдобёмита и байерита. После нагревания как оболочки так и обособившиеся кристаллические фазы дали вещество со шпинелевой структурой, содержащее алюминий в тетраэдрической координации; при этом структура ядра не изменилась.

Предложенная модель может объяснить особенность растворения, фосфатную реакцию и каталитические свойства аморфных алюмокремниевых смесей.

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