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The Hydration and Crystallization of ρ-Alumina and Alumina-gel in Aqueous Solutions of Various Basic Reagents

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Alumina gel, boehmite gel, ρ-alumina, η-alumina, and γ-alumina were treated with aqueous solutions of various inorganic and organic reagents at temperatures below 100°C. Boehmite gel, η-alumina and γ-alumina were found to show no change upon this treatment, while alumina gel and ρ-alumina either remained unchanged or changed into fairly well-crystallized boehmite, boehmite gel, gibbsite, bayerite, or nordstrandite, according to the treating conditions. It has been newly established that water-containing pyridine and aniline, the aqueous solution of hydrazine hydrate, and the aqueous solution of *o, m*-phenylenediamine are effective in forming fairly well-crystallized boehmite, nordstrandite, and gibbsite respectively.

A precipitate obtained from an aluminum salt aqueous solution by neutralization with ammonia and dried at a low temperature is found to be amorphous by X-ray analysis. The present authors have designated it as "alumina gel." Willstätter[1] had designated such an amorphous gel as C_α-gel; he also designated the precipitate which showed diffused boehmite-like X-ray diffractions as C_β-gel, and the one which showed X-ray diffractions of bayerite as C_γ-gel. He had described the occurrence of these gels as being dependent on the neutralization conditions and said that C_α-gel had a tendency to change into C_β-gel, and then gradually into C_γ-gel. These experimental results have been confirmed by several succeeding investigators. In this paper, C_β-gel will be called "boehmite gel."

Nordstrand[2] found a new aluminum trihydroxide, "nordstrandite," which was different from gibbsite and bayerite in the stacking sequence of its layer structure.[3] Afterward nordstrandite was found to occur in nature[4] and was also synthesized by treating alumina gel with an aqueous solution of ethylenediamine.[5]

Funaki *et al.*[6] studied the aging process of alumina gel and presented a mechanism whereby three crystalline hydrates and one gelatinous hydrate were formed independently. However, they did not describe the favorable conditions for each process.

→ gibbsite
alumina gel — → bayerite
→ nordstrandite
→ boehmite gel

As for the aging of ρ-alumina, Tertian[7] reported that ρ-alumina had a tendency to change into bayerite upon rehydration.

In this experiment the present authors aged ρ-alumina and alumina gel with aqueous solutions of organic and inorganic basic reagents at temperatures below 100°C. Boehmite gel, η-alumina, and γ-alumina were also treated under the same conditions, but no reaction was observed with them.

Specimen

Alumina Gel. An $AlCl_3$ aqueous solution of 0.5 mol/*l* was treated with a 14% aqueous solution of ammonia in order to adjust the pH to 8.0. The alumina gel thus obtained was then thoroughly washed and used in the wet state. This gel is amorphous to X-rays and contains about 5 mol of adhered and combined water per mole of Al_2O_3.

ρ-Alumina. Gibbsite was heated at 600°C in a vacuum (below 3 mmHg). The dehydrated

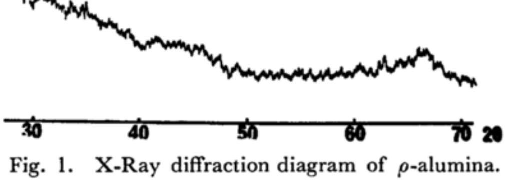

Fig. 1. X-Ray diffraction diagram of ρ-alumina.

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[1] R. Willstätter, H. Kraut and O. Erbacher, *Ber.*, **58B**, 2449 (1925).

[2] R. A. Nordstrand, *Nature*, **177**, 713 (1956).

[3] B. C. Lippens, "Structure and Texture of Aluminas," Proetschrift Delft, Netherlands (1961), p. 40.

[4] J. C. Hathaway and S. O. Schlanger, *Am. Mineralogist*, **50**, 1029 (1965).

[5] U. Hauschild, *Z. Anorg. Allg. Chem.*, **B24**, 15 (1963).

[6] Y. Funaki and Y. Shimizu, Preprint for the 12th Annual Meeting of the Chemical Society of Japan (April, 1959).

[7] R. Tertian and D. Papee, *J. Chem. Phys.*, **55**, 341 (1958).

alumina thus obtained gives the X-ray diffraction pattern shown in Fig. 1, a pattern which shows only one peak, at $d=1.40$ Å.

Experimental

Hydration. Alumina gel and ρ-alumina were treated with water, an NaOH aqueous solution, an NH_3 aqueous solution, various organic amines, and their aqueous solutions.

Identification. The identification was made by referring to the characteristic equistructural diffraction peaks of gibbsite and bayerite, shown in Fig. 2, and to the superstructural diffraction peaks of nordstrandite, shown in Fig. 3. Boehmite gel was identified from its three broad diffraction peaks, shown in Fig. 4.

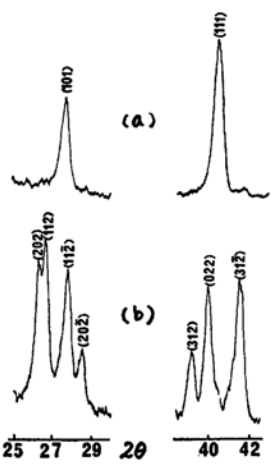


Fig. 2. X-Ray diffraction diagrams of bayerite (a) and gibbsite (b).

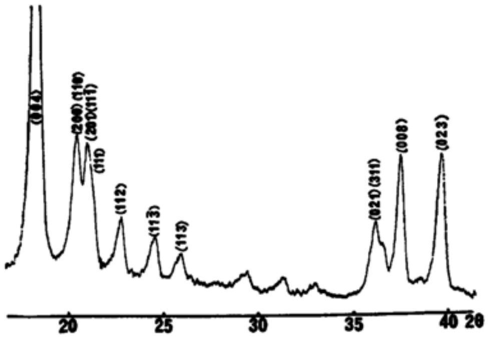


Fig. 3. X-Ray diffraction diagram of nordstrandite.

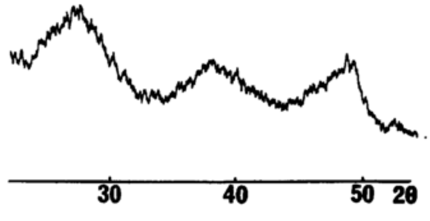


Fig. 4. X-Ray diffraction diagram of boehmite gel.

Results

The conditions of the hydration and the results of identification are shown in Table 1. The X-ray diffraction patterns of some typical specimens are shown in Fig. 5, Fig. 6, Fig. 7, and Fig. 8.

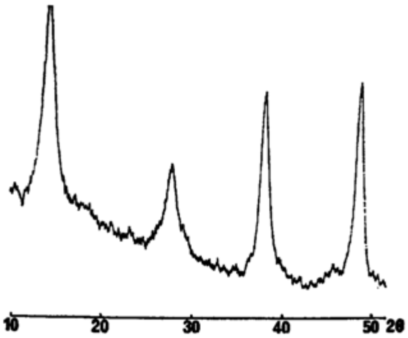


Fig. 5. X-Ray diffraction diagram of boehmite. (Condition: 95% Pyridine aq. soln., ρ-alumina, 70°C, 3 day. No. 39)

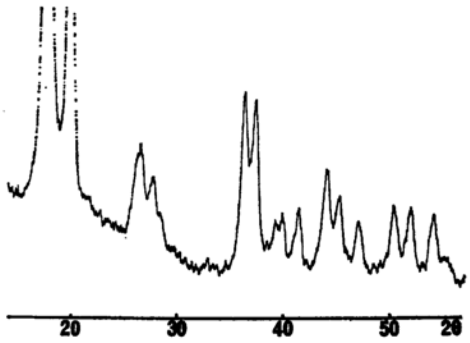


Fig. 6. X-Ray diffraction diagram of gibbsite. (Condition: *m*-Phenylenediamine sat soln., gel, 40°C, 15 day. No. 64)

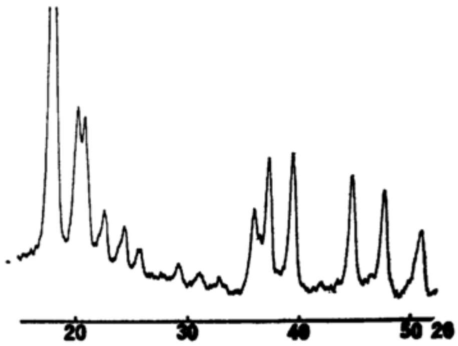


Fig. 7. X-Ray diffraction diagram of nordstrandite. (Condition: 5% Ethylenediamine aq. soln., gel, 40°C, 2 day. No. 69)

TABLE 1

Aging solution		Starting material	Temp. °C	Period day	Result	No.
H_2O	pH≒7	ρ	70, 50, 40 30	3	bo gel + bay	1
				15	bay + sq bo gel	2
			15	15	bay + bo gel	3
		gel	70, 50, 30	3	bo gel	4
			15	10	bo gel	5
	pH≒6		15	60	gel	6
6 N NaOH		gel	70	3	gib + bo gel	7
2 N NaOH					bo gel + vsq gib	8
0.1 N NaOH					bo gel	9
		gel, ρ	50, 30, 15	3	bay	10
NaOH aq. Soln.	$pH > 10$	gel	room temp.	60	bay	11
	$pH = 10—8$				bay + nor	12
	$pH = 8—7$				bay + bo gel	13
14% NH_4OH, 1 N Na_2CO_3		gel	50, 30, 15	3	bay	14
NH_4OH or Na_2CO_3 aq. soln.	$pH > 10.5$	gel	room temp.	60	bay	15
	$pH = 10.5—8.5$				bay + nor	16
	$pH = 8—7$				bo gel + bay	17
$(C_2H_5)_2NH$		gel	70, 60	30	bo	18
			50, 40, 30	3	bay > nor	19
			15	15	bay + sq bo gel	20
50% $(C_2H_5)_2NH$ soln.		ρ	50, 30, 15	3	bay	21
		gel	60	20	bo gel + vsq bay	22
			50, 40, 30	3	bay + bo gel	23
			15	15	bay + bo gel	24
10% $(C_2H_5)_2NH$ soln.		ρ	50, 40, 30	3	bay	25
			15	3	bay + bo gel	26
				15	bay + sq bo gel	27
		gel	50, 40, 30	3	nor + bay	28
5—10% $(C_2H_4OH)_2NH$ soln.		ρ	60, 40, 30	10	ρ + bo gel + sq gib	29
				30	gib + sq bo gel	30
		gel	60, 40, 30	30	bo gel	31
			15	3	gel + bo gel	32
				20	bo gel + bay	33

TABLE 1 (Continued)

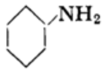
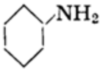
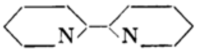
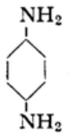
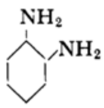
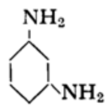
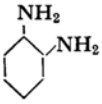
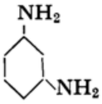
Aging solution	Starting material	Temp. °C	Period day	Result	No.
	ρ	70, 50, 30 15	20	ρ	34
	gel	70, 60	30	bo gel	35
		40, 30	3	gel + sq gib	36
			30	gib + bo gel	37
		15	30	bo gel + bay	38
85—95%  soln.	ρ	70, 60, 50	3	bo	39
		40, 30	3	bo + ρ	40
			20	bo	41
		15	20	bo gel	42
50%  soln.		70, 60, 50	3	bo + sq bay	43
		40, 30	5	bay + bo	44
		15	10	bo gel + sq bay	45
		70, 50, 40 15	20	ρ	46
96—97%  soln.	gel, ρ	70, 60, 50	3	bo + sq bay	47
		40, 30	10	bo gel + sq bay	48
		15	20		
 sat soln.	gel	40, 30, 15	20	gel	49
	ρ			bay	50
 sat. soln.	gel	60	30	gel + sq (bay + gib)	51
		50, 40, 30	3	gel + sq (bay + gib)	52
			15	gib + sq bay	53
		15	3	bay + sq gel	54
			15	bay	55
	ρ	60, 40, 30	3	bay	56
		15	3	bay + ρ	57
			20	bay	58
 and  sat. soln.		60, 40, 30	3	bay	59
		15	3	bay + ρ	60
			20	bay	61
	gel	60	30	bo gel	62
		50, 40, 30	3	gel + sq gib	63
			15	gib	64

Table 1 (Continued)

Aging solution	Starting material	Temp. °C	Period day	Result	No.
 and  sat. soln.	gel	15	3	bay + sq gib	65
			15	bay	66
$H_2NC_2H_4NH_2$	ρ	70, 50, 30 10	30	ρ	67
1—20% $H_2NC_2H_4NH_2$ soln.	gel, ρ	60	30	nor + bo gel	68
		50, 40, 30	2	nor	69
		15	5	nor (20 days for ρ)	70
0.1% $H_2NC_2H_4NH_2$ soln.	gel	50, 40, 30	30	gel + sq nor	71
5% $H_2NC_2H_4NH_2$ soln. 50 28% NH_4OH soln. 1	gel	40	3	nor	72
$H_2NC_2H_4NH_2$ 1 28% NH_4OH soln. 19				nor > bay	73
$H_2NC_2H_4NH_2$ 1 14% NH_4OH soln. 19				nor ≒ bay	74
$H_2NC_2H_4NH_2$ 1 14% NH_4OH soln. 99				bay + vsq nor	75
30—80% $H_2NNH_2H_2O$ soln.	gel, ρ	60	30	bo + gel + sq nor	76
		50, 40, 30	2	nor	77
		15	10	nor (20 days for ρ)	78
20% $CO(NH_2)_2$ soln.		60	30	bo + sq bay	79
		50, 30, 15	20	bo gel + bay	80
10% $(C_2H_4)(NH)_2(C_2H_4NH_2)_2$ and $NH(C_2H_4NH_2)_2$ soln.		60	7	bo gel + nor + bay	81
		50, 40, 30	2	bay + sq nor	82
		15	2	bay	83
	gel	60	7	bo gel + nor + bay	84
		50, 40, 30	2	nor + bay	85
		15	2	bay + vsq nor	86

gel: wet-alumina gel, ρ: ρ-alumina, gib: gibbsite, bay: bayerite, nor: nordstrandite, bo: boehmite, bo gel: boehmite gel, sq: small quantity, vsq: very small quantity

Discussion and Conclusion

1) Boehmite gel, η-alumina, and γ-alumina did not change under any conditions, so it is clear that they are stable enough under treatment with basic reagents at temperatures below 100°C.

2) Alumina gel and ρ-alumina behaved almost the same under all conditions, but when treated with unhydrous reagents, the different water contents of alumina gel and ρ-alumina were found to cause some differences in their crystallization processes.

3) As for alumina gel and ρ-alumina, the observed phenomena can be classified into the following 6 types:

a. Starting material remains unchanged.
b. Starting material changes into fairly well-crystallized boehmite.
c. Starting material changes into boehmite gel.
d. Starting material changes into bayerite.
e. Starting material changes into gibbsite.

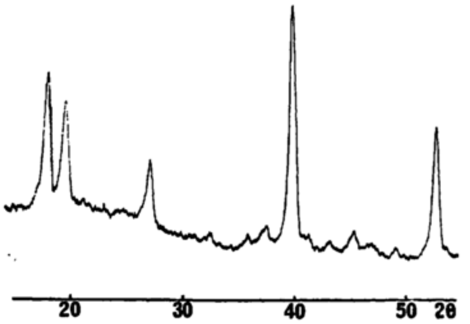


Fig. 8. X-Ray diffraction diagram of bayerite. (Condition: 10% Triethylenetetramine aq. soln., ρ-alumina, 15°C, 2 day. No. 83)

f. Starting material changes into nordstrandite.

4) ρ-Alumina remained unchanged when treated with unhydrous reagents, as in No. 34, No. 46, and No. 67; no similar phenomenon was observed in alumina gel, however since it contains a considerable amount of water. Alumina gel remained unchanged in No. 6 and No. 49. No. 6 shows that the crystallization of alumina gel does not proceed in such a sligtly acidic aqueous solution. The reason for No. 49 is not clear.

5) The "b" phenomena are caused by treating ρ-alumina at rather high temperatures with pyridine and aniline which contain a small amount of water, as in cases of No. 39, No. 40, No. 41, No. 43, and No. 47, and by treating alumina gel with a α, α'-diphenylamine aqueous solution and with aniline which are pure or which contain some water, as in cases of No. 18, No. 22, and No. 47.

From these results, the most favorable conditions for fairly well-crystallized boehmite formation seem to be a rather large solubility of the alumina and a low activity of the water.

6) The "c" phenomena are caused by treating alumina gel with pure water at any temperature and with slightly basic reagents at rather high temperatures, as in cases of No. 4, No. 5, No. 9, No. 31, and No. 35. However, the pure boehmite gel can not be obtained from ρ-alumina under the same treatment except in the cases of No. 1, No. 42, and No. 45.

These results can be attributed to the different solubilities of alumina gel and ρ-alumina. The solubility of ρ-alumina is larger than that of alumina gel. A favorable condition for forming boehmite gel is a rather small solubility. The solubility of ρ-alumina is too large and the temperature conditions of No. 42 and No. 45 are too low for forming fairly well-crystallized boehmite, so boehmite gel has been formed under these conditions.

7) The "d" phenomena are caused by conditions of large alumina solubility, high water activity, and comparatively low temperatures, as in the cases of No. 10, No. 11, No. 14, No. 15, No. 20, No. 21, No. 25, No. 50, No. 55, No. 56, No. 58, No. 59, No. 61, No. 66, No. 83, and No. 86.

The effect of low temperatures on bayerite formation can be sufficiently observed in the cases of No. 10, No. 20, No. 55, No. 66, No. 83, and No. 86. This effect is also observed in the Bayer process, in which gibbsite is formed at higher temperatures and bayerite, at lower temperatures.

The effect of solubility is confirmed from the fact that ρ-alumina changes more easily into bayerite than does alumina gel under the same conditions.

8) The "e" phenomena are found in the cases of No. 7, No. 30, No. 37, No. 53, and No. 64, but only in No. 64 are conditions sufficient for forming pure gibbsite. The conditions of No. 7 somewhat resemble those of the Bayer process; these conditions are a rather larger solubility and a high temperature. The conditions of No. 64, treating alumina gel with an *o*, *m*-phenylenediamine aqueous solution, constitute a new method for gibbsite formation.

9) The "f" phenomena are found in the cases of No. 69, No. 70, No. 72, and No. 78. The effect of an ethylenediamine aqueous solution had already been established,[5] but that of a hydrazine hydrate aqueous solution is first established by our experiment.

10) The reason why bayerite, gibbsite, or nordstrandite is formed selectively under treatment with a certain basic reagent is very interesting, but it can not be well explained now, remaining as a problem for furture study. This effect is possibly related to the molecular structures of the basic reagents.