ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. VII. THE RELATION BETWEEN THE CONSTITUENTS OF THE EARTH AND ITS CATALYTIC ACTION.*

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It has been shown in the previous papers(1) that Japanese acid earth has various catalytic actions on various organic compounds. The earth is, however, not a definite compound and it seems most probable that it is essentially a kind of hydrated aluminium silicate mixed with colloidal silica(2) and small amounts of many other metallic oxides. Still it remains unknown which of these constituents plays a principal part in its characteristic actions except that it owes its oxidase-like actions to the minute quantity of manganese dioxide contained in it(3).

When a mixture of naphthalene and some dry powdered acid earth was heated at about 300° in a sealed tube, a marked amount of a resinous matter was produced, which was found mainly composed of β, β'-dinaphthyl. The rôles played by the chief constituents of the earth in this catalytic action were investigated in the present experiment.

The Resinous Matter. The reaction product in a sealed tube was extracted with benzene. After the benzene was distilled off the residue was distilled in steam to remove unchanged naphthalene, when a mass of chocolate colour was left behind in the distillation flask. About 70 per cent. of this resinous matter passed over between 260° and 310° under 28 mm., and solidified at once to a yellow crystalline mass. It was recrystallized several times from alcohol with the addition of animal charcoal. The colourless scales of β, β'-dinaphthyl were obtained, which melted at 182° when heated alone or with the authentic specimen synthesized from β-chloronaphthalene.

The earth after complete extraction with benzene has a grey colour and its weight increase is always 1–2 per cent. of the resinous matter produced,

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(1) Inoue, This Bulletin, **1** (1926), 157, 177, 197, 219; **9** (1934), 353; Inoue and Ishimura, ibid., **9** (1934), 423.

(2) Yamamoto, *J. Soc. Chem. Ind. Japan*, **34** (1931), 244 B; ibid., **36** (1933), 38 B, 460 B.

(3) Kameyama and Oka, *J. Soc. Chem. Ind. Japan*, **33** (1930), 335 B; Iimori, *Bull. Inst. Phys. Chem. Research, Japan*, **9** (1930), 852.

and no other product is found. The yield of the resinous matter depends largely upon the temperature and the duration of the reaction as well as the amount and pre-treatment of the earth, yet it remains constant within about ±2 per cent. under a definite condition, and it can, therefore, be taken as a direct measure of the catalytic activity of Japanese acid earth on naphthalene.

The Standard Condition. The standard condition to measure the catalytic activity was chosen as follows: 25.00 g. of "pure naphthalene" from Tokyo Gas Co., Ltd. (sulphur content 0.05 per cent.) and 6.25 g. (25 per cent. of the naphthalene) of the dry earth were mixed and charged in a glass tube of 50–70 cm. in length and 2 cm. in diameter. The tube was sealed and heated in an electric furnace. The earth used had been dried at 120° for one hour, powdered, sifted with a sieve of 200 meshes, and heated once more at 300° for one hour. The temperature of the furnace was gradually raised to 300° in the course of just one hour and a half and maintained there for one hour. Then the electric current was cut off and the furnace was left to cool down to room temperature.. The content of the sealed tube was washed out with benzene, and filtered by a silk sack. The earth in the sack was then completely extracted with benzene in a Soxhlet apparatus for 8–30 hours. The two benzene extracts were united and filtered, the benzene was distilled off, and the residue was subjected to steam distillation to remove unchanged naphthalene. The resinous matter left behind in the distillation flask was collected, rinsed out with benzene if it sticked to the wall of the flask, in a small weighed beaker, and dried at 120° until a constant weight to 0.01 g. was obtained.

The Relation betweeen the Yield of the Resinous Matter and Chemical Composition of the Acid Earth. Seven specimens of the acid earth were analysed on one hand and their catalytic activities under the "standard condition" were measured on the other hand. The results are shown in Table 1.

No relation between the chemical composition and the catalytic activity seems to be found out from Table 1. But, when we take the ratios of the percentages of other constituents to those of SiO_2 as shown in Table 2, distinct relations between them and the catalytic activities can be found: (1) the larger the value of Al_2O_3/SiO_2, the greater the catalytic activity; (2) the larger the values of CaO/SiO_2 and K_2O/SiO_2, the smaller the catalytic activity; and, (3) the values of Ig. loss/SiO_2, Fe_2O_3/SiO_2, and MgO/SiO_2 seem to have no relation to the activity.

Table 1.

Earth	Locality of production	Depth of deposit where sample was gathered (metres)	Chemical composition (%)								Yield of resinous matter (g.)
			Ignition loss	SiO_2	Al_2O_3(5)	Fe_2O_3	CaO	MgO	K_2O(4)	Total	
A	Isozawa	7	9.51	65.62	13.61	3.89	1.47	3.98	1.82	99.90	1.65
B	Isozawa	3	7.78	67.91	16.09	3.17	0.60	3.51	1.35	100.41	1.82
C	Itoigawa	6.5	10.45	68.18	14.95	2.53	1.11	1.20	1.02	99.44	1.86
D	Odo-Sekiba	4.5	6.98	72.34	13.73	3.37	1.18	1.28	1.04	99.92	1.90
E	Odo-Sekiba	1.2	8.84	65 69	18.47	2.65	0.79	2.08	1.17	99.69	2.10
F	Itoigawa	Commercial	6.87	67.04	17.71	1.57	0.40	4.99	0.63	99.32	2.23
G	Itoigawa	0.9	11.50	58.92	20.13	3.05	0	3.15	0.95	97.70	2.60

Table 2.

Earth	$\frac{\text{Ig. loss}}{SiO_2}\times 100$	$\frac{Al_2O_3}{SiO_2}\times 100$	$\frac{Fe_2O_3}{SiO_2}\times 100$	$\frac{CaO}{SiO_2}\times 100$	$\frac{MgO}{SiO_2}\times 100$	$\frac{K_2O}{SiO_2}\times 100$	Yield of resinous matter(g.)
A	14.5	20.7	5.93	2.24	6.07	2.77	1.65
B	11.5	23.7	4.67	0.88	5.17	1.99	1.82
C	15.3	21.9	3.71	1.63	1.76	1.50	1.86
D	9.7	19.0	4.66	1.63	1.77	1.44	1.90
E	13.5	28.1	4.03	1.20	3.17	1.78	2.10
F	10.1	26.4	2.33	0.60	7.44	0.94	2.23
G	19.5	34.2	5.18	0	5.35	1.61	2.60

The problem was then attacked from another side; each constituent was considered separately and investigated on its catalytic activity for naphthalene.

SiO_2 and Al_2O_3. Silicic acid gel and aluminum hydroxide prepared by various methods were examined in the first place. The results are shown in Table 3.

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(4) Na_2O was weighed together with K_2O.

(5) It has been already pointed out by Okazawa that Al_2O_3 content is always larger in the upper layers of Japanese acid earth deposits than in the lower, which may be noticed here again. (*Bull. Inst. Phys. Chem. Research, Japan,* **7** (1928), 977.)

Table 3.

	Method of preparation	Yield of resinous matter (g.)	Remarks
SiO_2 gel	(a) Dil. solution of $Na_2Si_2O_5 \cdot 2H_2O$ into 2.8 N nitric acid.	0.03	The quantity of the catalyst, 12.5 g. instead of 6.25 g. Standard condition in other respects.
	(b) Dil. solution of water glass into dil. hydrochloric acid.	0.06	Under the standard condition.
	(c) Ferric chloride solution into water glass solution. (Holmes's gel)(6)	0.03	,,
	(d) Holmes's gel washed with hydrochloric acid.	0.01	,,
$Al(OH)_3$(7)	(a) Clay was treated with sulphurous acid and resulting aluminium sulphite was decomposed by boiling.	0.00	The quantity of the catalyst, 12.5 g.
	(b) Dil. aqueous ammonia into dil. solution of aluminium nitrate.	0.02	Under the standard condition.
	(c) Dil. aqueous ammonia into dil. solution of aluminium chloride.	0.00	,,

As shown in Table 3, all the specimens of silicic acid gel and aluminium hydroxide used alone manifest no or quite poor activity. But when the two substances are mixed together in a suitable manner, a remarkable amount of the resinous matter is produced, the activity of the mixed catalyst becoming comparable to that of the acid earth.

Silicic acid gel (a) and aluminium hydroxide (b) of Table 3 are suspended in water separately, about 0.2 g. as SiO_2 or Al_2O_3 being contained per 10 c.c., and the two suspensoids are mixed in a porcelain basin, and evaporated to dryness on the water bath under stirring. The dried mass is powdered, treated as the "standard condition" requires, and tested on its catalytic activity. The yield of the resinous matter produced by the mixed catalyst thus obtained are plotted against the composition of the mixture in Fig. 1. The "standard condition" was adopted in the experiments except that 5.00 g., instead of 6.25 g., of the mixed catalyst was always taken.

Fig. 1 shows that there is a maximum in the catalytic activity in the neighbourhood of the composition, 35 per cent. Al_2O_3 and 65 per cent. SiO_2,

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(6) Holmes, *Ind. Eng. Chem.*, **17** (1925), 280; ibid., **18** (1926), 386.

(7) Aluminium hydroxide, as it is very troublesome to wash completely, was finally purified by electro dialysis.

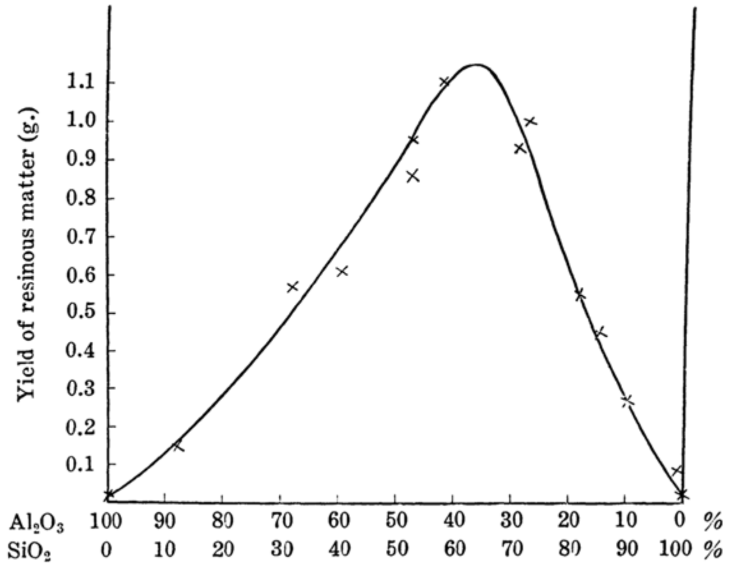

Fig. 1.

which corresponds to $Al_2O_3 \cdot 3SiO_2$. Its position, however, may be shifted according to the method of the preparation of silicic acid gel and aluminium hydroxide and the manner of mixing them. Moreover, it is not explicit whether any definite compound is formed by the simple mixing of the two, and, even if it is actually formed, it cannot be at once taken for granted that its composition and that of the constituent of the acid earth possessing the catalytic activity are identical. Notwithstanding that, it is evident that the co-existence of SiO_2 and Al_2O_3 is essential to the catalysis, and at any rate it is possible to prepare a catalyst with the activity comparable to that of the acid earth by the simple mixing of the above mentioned two substances, each of which is an extremely weak agent for the action when used alone, and the parallelism between the values of Al_2O_3/SiO_2 and catalytic activities shown in Table 2 seems to be not unreasonable from the above experimental results.

As already stated, if the acid earth contains free colloidal silica, the catalytic activity of such an earth with a comparatively small content of Al_2O_3 may be raised by adding aluminium hydroxide to it, for catalytically active centres may be newly formed. On the contrary, the addition of silica gel would result only in the dilution of the catalyst and cause the lowering of activity. Experimental results are in close agreement with the above speculation. The acid earth (A) of Table 1 was kneaded with a little water to a paste, diluted with water, and fresh aluminium hydroxide (as

Al_2O_3 about 10 per cent. of the weight of the earth dried at 300°) suspended in water was added to it. The whole was then evaporated to dryness on the water bath under stirring. This mixture used under the "standard condition" yielded 1.95 g. of the resinous matter. The increase in the yield of the product is about 20 per cent. (refer to Table 1 and 2). By the similar treatment the activity of the acid earth (C) of Table 1 was raised by about 15 per cent., whilst it was lowered by about 6 per cent., when the earth was mixed with silica gel (10 per cent. as SiO_2).

Hydroxides of Alkali and Alkaline Earth Metals. As stated above, the larger the ratios CaO/SiO_2 and K_2O/SiO_2 the smaller is the catalytic activity. It seems very probable, therefore, that the hydroxides of alkali and alkaline earth metals behave as poisons to the catalysts, and, as a matter of fact, this was the case. To the acid earth (F) of Table 1, a dilute solution of sodium hydroxide was added and the whole was evaporated up under stirring. Under the "standard condition" this contaminated catalyst gave no resinous matter when the quantity of the added hydroxide amounted to 5 per cent. of the weight of the dry earth, the catalytic activity being thus destroyed entirely, while the depression of the activity was 10 per cent. on the addition of 1 per cent. of the hydroxide. The acid earth (E) mixed with 3 per cent. of sodium hydroxide gave only 0.03 g. of the resinous matter (the depression is more than 98 per cent.). Potassium hydroxide is a stronger poison; with 1 per cent. of the hydroxide the activity of the earth (D) was lowered by about 20 per cent.

The action of the hydroxides of alkaline earth metals is milder; the acid earth (F) with 5 per cent. (as CaO) of calcium hydroxide gave 0.24 g. of the resinous matter, the depression of the activity being about 90 per cent., and with 3 per cent. of CaO the activity of the acid earth (F) was lowered by about 50 per cent. The intensity of the poisoning by barium hydroxide is nearly equal to that by calcium hydroxide.

It was further observed that, when the poisoned earth was treated with hydrochloric acid, it recovered the original activity completely.

Ferric and Magnesium Hydroxides. As seen from Table 2, the value of neither Fe_2O_3/SiO_2 nor MgO/SiO_2 has parallelism with the catalytic activity. It may be therefore anticipated that ferric and magnesium hydroxides are indifferent to the catalytic action.

Each hydroxide, prepared by the interaction of the nitrate and aqueous ammonia, washed with a large quantity of water, and purified finally by electro-dialysis, was suspended in water and added to the acid earth. The decrease in the yield of the resinous matter just matches that caused by the dilution of the catalyst as in the case of silica gel.

It was also found that no resinous matter was produced by the use of a mixture of silica gel and ferric hydroxide ($SiO_2 : Fe_2O_3 = 3:4$) and, as already stated, Holmes's silica gel containing ferric hydroxide prepared from water glass and ferric chloride manifested almost no activity. From the above results, it may be safely granted that Fe_2O_3 and MgO are the simple diluents of the catalyst.

Thus, it appears that the rôles played by the chief constituents of Japanese acid earth in its catalytic action on naphthalene are fully explained and experimental results are in close agreement with the expectation. Water plays also an important part in the catalysis and its action will be discussed in details in another communication.

The Activities of Several Substances other than Japanese Acid Earth. Several other substances were analysed and examined on their catalytic activities on naphthalene by the same method. The data of experiments are shown in Table 4.

Table 4.

Substance	Locality of production	Chemical composition (%)								Yield of resinous matter (g.)
		Ignition loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Total	
Bentonite	Japan	7.22	63.30	20.30	3.00	1.12	0.54	3.38	98.89	0.25
Caoline	Japan	12.42	50.19	32.79	3.10	0.35	0	1.34	100.19	0.81
Clay I	Manchukuo	13.87	45.38	34.29	4.80 (+ TiO_2)	1.43	1.11	—	—	0.33
Clay II	Manchukuo	14.54	43.56	40.36	2.21 (+ TiO_2)	0.79	0.34	0.95	102.75	0.20
Diatom earth	Japan	5.10	80.70	11.90	3.90	0	0.20	0	101.80	0.22
Bauxite	India	12.87	1.22	74.78	10.35 (+ TiO_2)	0.49	0.16	—	—	0
Active charcoal	Germany	—	—	—	—	—	—	—	—	0

All the substance, which contain SiO_2 and Al_2O_3 as their chief constituents, possess more or less the catalytic activity on naphthalene.

According to Shigemune(8), Japanese bentonite much resembles Japanese acid earth in its chemical composition, adsorptive powers for dyestuffs, and in many other respects, while Table 4 shows that its catalytic activity is only about one tenth of that of the acid earth. In the authors' opinion, its poor activity may be attributed to the comparatively large contents of CaO

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(8) *Reports of Tokyo Imperial Industrial Research Laboratory*, **25** (1930), No. 10.

and K_2O, both the strong poisons to the catalysis, and therefore, if these poisons be removed, the activity may be raised. On treating the acid earth with hydrochloric acid, its composition as well as its catalytic activity suffers little change. In the case of bentonite, however, the ratio $CaO+K_2O/SiO_2$ is greatly diminished by the same treatment (in this respect there is a distinct difference between the two) and simultaneously its activity is raised enormously as shown in Table 5, exceeding even the greatest value of the acid earth given in Table 1. This result seems to be anticipated if the data given in Table 2 and 5 are compared, and bentonite is regarded as a species of the acid earth so far as the catalytic action is concerned.

Table 5.

Catalysts		$\frac{\text{Ig. loss}}{SiO_2}\times 100$	$\frac{Al_2O_3}{SiO_2}\times 100$	$\frac{Fe_2O_3}{SiO_2}\times 100$	$\frac{CaO}{SiO_2}\times 100$	$\frac{MgO}{SiO_2}\times 100$	$\frac{K_2O}{SiO_2}\times 100$	Yield of resinous matter (g.)
Earth F	Before treatment with HCl	10.1	26.4	2.33	0.60	7.44	0.94	2.23
	After treatment with HCl	9.79	25.7	1.32	0.73	6.08	0.66	2.33
Bentonite	Before treatment with HCl	11.4	32.1	4.74	1.77	0.85	5.34	0.25
	After treatment with HCl	10.9	36.0	3.31	0.77	1.08	1.21	2.89

Further experiments were carried out to ascertain whether SiO_2 and Al_2O_3 could be replaced by TiO_2 and La_2O_3 respectively or not, and the combinations of TiO_2-Al_2O_3 and SiO_2-La_2O_3 were tested on the catalytic action. No resinous matter was found to be produced in both cases. Some interesting results might be attained if the above experiments be extended to various other metallic oxides.

Summary.

(1) Rôles played by the chief constituents of Japanese acid earth in its catalytic action on naphthalene have been studied. It has been found that the co-existence of SiO_2 and Al_2O_3 is essential to the catalysis and hydroxides of alkali and alkaline earth metals behave as poisons to the catalyst, while ferric and magnesium hydroxides are indifferent to the catalysis.

(2) Several substances other than Japanese acid earth, which contain SiO_2 and Al_2O_3 as their chief constituents, have been also examined on the same catalytic action.

(3) It has been tested whether TiO_2 and La_2O_3 can be substituted for SiO_2 and Al_2O_3 respectively in the catalytic action or not.

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