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ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. X. THE MECHANISMS OF THE PROMOTION AND POISONING OF THE CATALYTIC ACTION.*

By Koshiro ISHIMURA.

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The Mechanism of the Promotion. It has been suggested in a previous paper⁽¹⁾ that the co-existence of Al_2O_3 and SiO_2 is essential to the catalytic action of Japanese acid earth on naphthalene and all other metallic oxides are unnecessary for it. There has been, however, always present in the reaction system another component not to be overlooked, i.e. water. The earth heated at 500° still contains a few per cent. of water.(2) Isobe(3) observed that it retains a small amount of water even after heated at 1000° for six hours.

The earth dried at 300° rapidly adsorbs water vapour. A small fraction of this adsorbed water is held very firmly by the earth and cannot be set free at 120° even after the constant weight of the earth is obtained. This tenaciously held water has been called "retained water" by the present author(4) in order to distinguish it from adsorbed or added water. The molecules of the retained water may highly probably be those directly held by the bare surface of the earth. The catalytic activity of the earth is greatly promoted when it carries the retained water as described in details in the preceding paper. Therefore, it is very probable that the catalysis in question is performed by the three component catalyst consisting of Al_2O_3, SiO_2, and water; the molecules of naphthalene are activated when they are adsorbed on the catalytically active centres of these three components.

When the earth is heated at 300° some of these active centres lose molecules of water and consequently become inactive. They will, however, recover their ability if water molecules are put in their original positions, and this recovery of the catalytic activity is accomplished by the retained

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* An epitomized translation of the original published in Vol. 29 of the Reports of the Tokyo Imperial Industrial Research Laboratory.

(1) Inoue and Ishimura, This Bulletin, **9** (1934), 431.

(2) Ishimura, This Bulletin, **9** (1934), 522.

(3) Isobe, *J. Chem. Soc. Japan*, **51** (1930), 761.

(4) Ishimura, *loc. cit.*

water, giving rise to the observed promotion of the activity. The promotion would be therefore necessarily accompanied by the increase in the water content of the earth. On the contrary, if the promotion is caused by the increase in the surface area due to the prolonged exposure to water vapour in the same manner as many metals are activated by the adsorption of gases,(5) the promotive power would be a function of the time of adsorption or of the total amount of adsorbed water but not of the amount of retained water. The experimental results however contradict with the latter view. When water is adsorbed in the absence of air the adsorption proceeds much more rapidly and the ratios of retained water to the total amounts adsorbed are much greater than in the case of the adsorption in the open air. By comparing the promotive powers of the samples thus prepared with those given in Table 2 in Part IX of this series,(6) one comes at once to the conclusion that the promotive power is a function of the amount of retained water but not of the total amount adsorbed nor of the time of adsorption. Moreover, when the moist earth is dried at 120° under highly reduced pressure the amount of the retained water is diminished with the decrease in the promotive power.

Thus it is most probable that the existence of water is indispensable for the promotion of the catalytic activity.(7)

As always stated,(8) the retained water can be replaced by other neutral substances containing oxygen in their molecules such as alcohols, acetone, and ether. So, generally speaking, the catalytic action on naphthalene is effected by the three component catalyst consisting of Al_2O_3, SiO_2, and one of these substances mentioned above.

The Mechanism of the Poisoning. The poisons in this catalytic action can be classified into two distinct types: strong poisons such as ammonia, amine, nitrile, and amyl nitrite, and weak poisons such as hydrogen chloride and acetic acid. The mechanism of poisoning will be discussed separately about each type.

Though poisoning by ammonia is very drastic, its action is not fatal to the active centres. The catalytic activity will be restored completely if the adsorbed poison is all expelled. It is very difficult however to liberate the total ammonia retained. The complete liberation was attained only when

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(5) It is believed that molecules of gas diffusing through metal actually enter into metal lattice, distending it, breaking it, and thus activating the surface of the metal. Piper, *Trans. Faraday Soc.*, **24** (1933), 540.

(6) Ishimura, This Bulletin, **9** (1934), 523.

(7) It goes without saying that the promotion is not a mere annealing effect.

(8) Ishimura, *loc. cit.*

the poisoned earth was heated at 500° for two hours under the reduced pressure of 4 mm. The activity of the earth thus freed from the retained ammonia was compared with that of the original sample with the same heat treatment and there could be seen no difference between them.

The earth with the sufficient amount of the poison to cover the whole surface does not recover its activity by adsorbing water or alcohol. When, however, its surface is only partly covered by the poison and there is left an ample room to retain these oxygen-containing neutral substances, then the activity is increased to a marked degree by the adsorption of these substances. It seems therefore that the strong poisons are adsorbed selectively and strongly on the active centres, rendering them inactive for the catalysis.

This is not the case with the weak poisons such as hydrogen chloride and acetic acid. Though they are in themselves poisons their selection of the location of adsorption would be different; they are adsorbed first and retained to the very last on the inactive parts of the surface. Their poisoning effects are not therefore manifested unless their retained amounts are relatively large, and even if all the active centres are covered by them they may be liberated easily in the course of reaction, hence the weakness of their poisoning actions.

The amount of naphthalene adsorbed by the acid earth with the various retained substances are plotted against time as shown in Fig. 1.

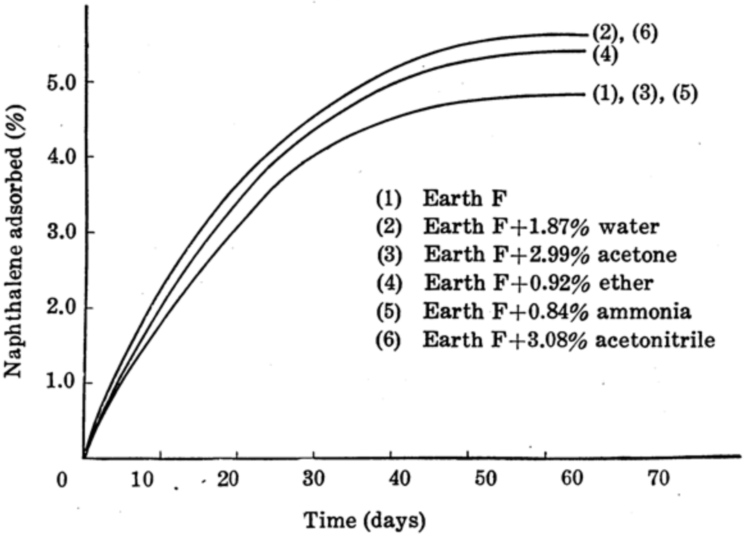

Fig. 1.

The adsorption experiment was carried out in the same manner as described in the previous paper.(9) Fig. 1 shows that the total amount adsorbed is not influenced appreciably by the retained substance, whether it is a promoter or a poison. Therefore the rôle of poisons does not consist in the prevention of the adsorption of naphthalene. They only render the catalytically active parts inactive before there occurs the adsorption of naphthalene. In other words, the adsorption of naphthalene is converted from the "chemical" into the "physical" by the poisons.

The Surface Area of the Acid Earth. The surface area per gram of the acid earth was calculated from the specific gravity and diameter of the particles of the earth. Kobayashi(10) measured the specific gravities of the dried earths and gave the values 2.7—2.9, while Isobe(11) 2.67—2.70. Recently Yamamoto(12) determined them again and found 2.4~2.5. The value 2.7 was taken in the present calculation. The diameter of the particles of the dried earth is presumed to be less than 10^{-5} cm. from the observation of X-ray patterns.(13) Isobe(14) determined it from the apparent and true specific gravities and the number of cracks on the surface of the earth observed by a microscope and found the value 2.35×10^{-5} cm., while Kobayashi(15) gave $3.3 \sim 6.2 \times 10^{-5}$ cm. by counting the number of particles suspended in water using an ultramicroscope and measuring the weight after evaporating up the water. The value 2×10^{-5} cm. was here adopted.

Let us assume that each particle is cubic in form with the sides of 2×10^{-5} cm. in length, then the surface area of one particle is 2.4×10^{-9} sq. cm. Since the specific gravity is 2.7, the number of particles contained in 2.7 g. is $(1/2^3) \times 10^{15} = 1.25 \times 10^{14}$, hence the number of particles per gram is 4.63×10^{13}. The total surface area per gram is therefore 1.11×10^5 sq. cm. $\fallingdotseq 10$ sq. m. This represents about one tenth of the surface area(16) of active charcoal.

As stated in the previous paper, when 0.49 millimol of ammonia is retained by one gram earth, the activity of the earth is entirely lost. Further experiment showed that by 0.15 millimol of ammonia retained by one gram earth the activity was decreased by 77 per cent. Adopting a

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(9) Ishimura, This Bulletin, **9** (1934), 498.

(10) Kobayashi, "Japanese acid earth," 2nd Ed. (1927).

(11) Isobe, *Sci. Pap. Inst. Phys. Chem. Research (Japan)*, **5** (1926), 175.

(12) Yamamoto, *Waseda Appl. Chem. Soc. Bull.*, No. **17** (1932), 2.

(13) Kameyama and Oka, *J. Soc. Chem. Ind. Japan*, **33** (1930), 307.

(14) *Loc. cit.*

(15) *Loc. cit.*

(16) Cude and Hullet, *J. Am. Chem. Soc.*, **42** (1920), 398; Lamb and Coolidge, *ibid.*, **42** (1920), 1168.

value of 6.06×10^{23} for the Avogadro constant and 1.6×10^{-8} cm. for a molecular diameter of ammonia, we obtain an area of 1.71×10^{4} sq. cm. to be covered by 0.15 millimol of ammonia on the assumption of a packed monomolecular layer. Therefore, the total area of the active centres per gram earth is 2.22×10^{4} sq. cm. or about 20 per cent. of the total surface area. This represents the greatest value possible, since the adsorption of ammonia is not necessarily quite selective and moreover the liberation of ammonia from the active centres may occur in the course of the reaction.

A simple calculation shows that the amount of water to cover the whole surface of the earth by a monomolecular layer would be about 2.5 per cent. of the weight of the dry earth, if the effective diameter of water molecule on the adsorption layer is 3.5×10^{-8} cm.(17)

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The Tokyo Imperial Industrial Research Laboratory,
Hatagaya, Tokyo.

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(17) This is not known accurately and must depend upon the orientation of molecules. It may be less than the above-mentioned value since it is probable that molecules on the adsorption layer are more closely packed than in liquid state.