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Adsorption of Phosphate on Synthetic Silica-Alumina Possessing Lewis-acid Sites

Kazuto TAKIMOTO, Akira FUJITA, and Satoru TSUDA
Department of Chemistry, Faculty of Engineering, Hiroshima University,
Senda-machi, Hiroshima 730

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Synopsis. It was confirmed from measurements of the adsorption isotherms of phosphates in aqueous solutions that there were adsorption sites with very high reactivity on the surface of silica–alumina. The concentration of adsorption sites which is estimated from the adsorption amount extrapolated to zero equilibrium concentration is nearly twice the concentration of Lewis-acid sites for silica–alumina of higher alumina content. Furthermore, the concentration of phosphate adsorbed on the surface of various silica–alumina is relatively well correlated with the concentration of Lewis-acid sites.

It is well known that inorganic phosphates play an important role in the abnormal growth of phytoplankton in an area of the sea or a lake, which is called red tide. Nishimura[1] has reported that the average concentration is 0.015 ppm for P and 0.14 ppm for N in a given sea area. The pollution source of the phosphates is mainly domestic sewage. Even in the effluent of so-called secondary sewage treatment, phosphate in concentrations of 3 to 5 ppm as P is usually detected.[2] Complete phosphate removal, which is relatively easy and economical compared with that of nitrogen, may offer the best solution for returning aquatic environments to their pristine state.[3] Although many workers have widely studied phosphate removal,[4–6] some clay minerals containing aluminium atoms are reported to be effective for the removal of phosphate at the very low concentrations described above. The aluminium atoms responsible for the phosphate removal are not the internal atoms of the adsorbent but the surface atoms. Therefore, it is expected that the concentration of Lewis-acid sites associated with surface aluminium atoms correlates with that of the phosphate adsorbed. To the authors' knowledge, no work has been done from such a viewpoint.

In the study reported here, synthetic silica–alumina samples having strong Lewis-acid sites, which also react with electron-donating polyaromatic hydrocarbons[7] were used as adsorbents. The object of the present paper is to clarify the correlation between the concentration adsorbed of Lewis-acid sites, the concentration of phosphate and the alumina content of the silica–alumina samples.

Experimental

Aluminium isopropoxide and tetraethyl orthosilicate purified under reduced pressure were mixed in various proportions and were hydrolyzed for 12 h. The gels thus obtained were treated at 600 °C for 8 h. The particles which passed through 100 mesh sieve were used as adsorbents. Each silica–alumina sample is represented as % silica–alumina which indicates the alumina content in wt%. The surface area of these silica–alumina samples were measured by means of the BET method. The concentration of Lewis-acid sites on the surface of the silica–alumina samples was measured by the Leftin method,[8] after heating *in vacuo* at 400 °C for 2 h.

The phosphate was adsorbed onto various silica–alumina samples at 20 °C. The adsorbents were suspended in aqueous KH_2PO_4 solutions having concentrations in the range from 1 to 10 mmol/l and the mixture were stirred for 48 h. It was confirmed that the adsorption equilibrium was reached within 48 h. After centrifugation, the phosphate concentration in the supernatant solutions was determined by the molybdenum blue method.[9]

Results and Discussion

The isotherms for the adsorption of phosphate onto the silica–alumina samples are shown in Fig. 1. The phosphate is only slightly adsorbed on samples ranging from pure silica gel to 25% silica–alumina, whereas adsorption clearly occurs on samples ranging from 40% silica–alumina to pure alumina. Thus, adsorption is enhanced with increasing alumina content. For pure alumina, however, the adsorption concentration, is slightly lower than that for 90% silica–alumina.

The phosphate adsorption concentration is fairly large even near zero equilibrium concentration in the cases from 50% silica–alumina to pure alumina. This result suggests that highly reactive sites responsible for the adsorption exist on the surface.

In order to confirm this, the Muljadi adsorption isotherm[10] and the Langmuir isotherm for alumina are shown in Fig. 2. The Langmuir theory assumes that all the adsorption sites are equivalent. This theory is

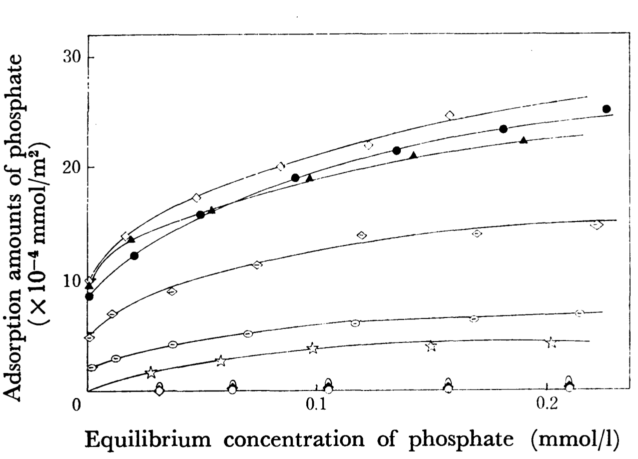

Fig. 1. Adsorption isotherms of phosphate on the surface of silica–alumina (S.A).
▲: Alumina, ◇: 90% S.A, ●: 75% S.A, ⟐: 60% S.A, ⊖: 50% S.A, ☆: 40% S.A, 0: 25% S.A, ◆: 10% S.A, ○: silica gel.

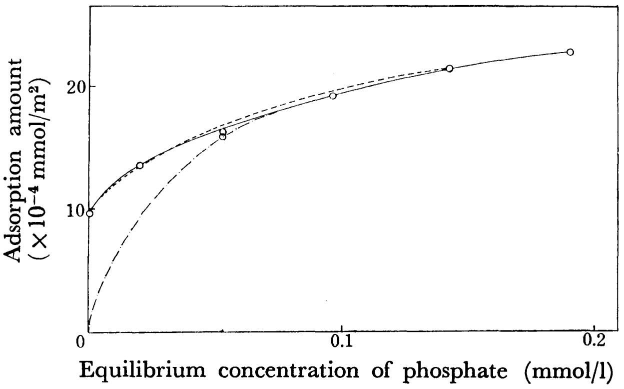

Fig. 2. Adsorption isotherms of phosphate on the surface of alumina.
—○—: Observed adsorption isotherm, —·—·: Langmuir adsorption isotherm, ----: Muljadi adsorption isotherm.

not applicable to the present results obtained at low phosphate concentrations. On the contrary, the adsorption isotherm obtained is in rather good accord with the Muljadi isotherm. Muljadi and his co-workers[10] have revealed that there are two types of adsorption sites on the surface of kaolinite, gibbsite and pseudoboehmite.

The concentration of highly-reactive sites estimated from the phosphate adsorption concentration extrapolated to zero equilibrium concentration is shown in Table 1. Since the reactive sites responsible for the adsorption are essentially surface aluminium atoms, it can be expected that the concentration of Lewis-acid sites is a good parameter for estimating the phosphate adsorption. The Lewis-acid sites associate with bare aluminium atoms due to the removal of water which is produced by a reaction between adjacent hydroxyl groups on the surface. The concentration of highly-reactive sites is nearly twice that of Lewis-acid sites for silica–aluminas of higher alumina content. This difference may be due to the following reason: there are weakly and strongly-bonded hydroxyl groups on the surface of silica–alumina, corresponding to strong and weak basic sites, respectively.[11] The phosphate can easily exchange with weakly-bonded hydroxyl groups in the aqueous solution, forming a surface complex with aluminium atoms. In the case of the strongly bonded groups, the ability of the phosphate to exchange with the hydroxyl groups may be less.

On the other hand, the weakly-bonded hydroxyl groups may be preferentially eliminated by heat treatment at 400 °C for 2 h *in vacuo*, forming weak Lewis-acid sites. All hydroxyl groups on the surface are not eliminated by the heat treatment.[12] Therefore, it is believed that strongly-bonded hydroxyl groups which form Lewis-acid sites with difficulty, have possibly an exchange ability in the aqueous solution, although this ability is weak. Another reason may be the positively-charged spots proposed by Cloos *et al.*[13]

TABLE 1. THE RELATION BETWEEN THE CONCENTRATION OF PHOSPHATE ADSORBED AND THE CONCENTRATION OF LEWIS-ACID SITES

Silica–alumina	Specific surface area (m^2/g)	Concentration of phosphate adsorbed ($\times 10^{-4}$ mmol/m^2)	Concentration of Lewis-acid sites ($\times 10^{-4}$ mmol/m^2)
Alumina	164.3	8.95	4.72
90% S.A	323.6	9.47	4.02
75% S.A	178.4	8.42	3.41
60% S.A	142.7	4.21	1.99
50% S.A	343.7	1.89	1.89
40% S.A	97.4	0.42	1.80
25% S.A	118.5	0	0.88
10% S.A	309.1	0	0.34
Silica gel	378.9	0	0.13

Table 1 indicates that the concentration of Lewis-acid site increases with the alumina content in silica–alumina. However, the adsorption concentration is zero up to 25% silica–alumina and, thereafter, it increases with the alumina content. This should be due to the negatively-charged surface caused by the isomorphous replacement of four-fold coordinating aluminium atoms into the tetrahedral silica framework. As the alumina content in silica–alumina is increased, the surface negativity decreases due to the increase in Al–OH cations with alumina content.[13]

Reference

1) H. Nishimura, *Kagaku*, **45**, 49 (1973).
2) F. Mukai, Japan Patent, Kokai 74-81290 (1975); *Chem. Abstr.*, **82**, 64087J (1975).
3) J. C. Goldman, *Water Res.*, **10**, 97 (1973).
4) R. Coleman, *Soil Sci. Soc. Am., Proc.*, **7**, 134 (1943).
5) K. R. Kar, *J. Sci. Ind. Res. (India)*, **17B**, 175 (1958).
6) Y. Ouikura, *Kyushu Nogyo Shikensho Iho.*, **9**, 51 (1963).
7) K. Takimoto and M. Miura, *Bull. Chem. Soc. Jpn.*, **44**, 1534 (1971); *ibid.*, **45**, 2231 (1972).
8) H. P. Leftin and E. K. Hall, *Actes Deuxième Congr. Int. Catal. Paris.*, Vol. I (a) p. 1353, (b) p. 1307.
9) Japanese Industrial Standards, K0102-1971.
10) D. Muljadi, A. M. Posner, and J. P. Quirk, *J. Soil Sci.*, **117**, 212 (1966).
11) K. Takimoto, *Bull. Chem. Soc. Jpn.*, **45**, 2391 (1972).
12) T. Morimoto, M. Nagao, and J. Imai, *Bull. Chem. Soc. Jpn.*, **44**, 1282 (1971).
13) P. Cools, A. Herbillon, and J. Echeverria, *Trans., Int. Congr. Soil Sci., 9th*, **2**, 733 (1968).