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ADSORBENT PHOSPHATES

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A Simple Explanation of the Figures

Figure 1 shows the relationship between the ratio area and composition ratio of the portions of raw materials at the time of manufacture. The second figure shows the effects of the heating conditions during the dehydration on the ratio area. Figure 3 indicates the gas chromatograph adsorption.

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A Detailed Explanation of the Invention

This invention is an adsorbent which uses as its main ingredient metallic phosphoric acid salts of Periodic Table group IV section A with large ratio areas of over  $150\text{m}^2/\text{g}$  which were obtained through a reaction between soluble group IV section A metallic salts and phosphoric acid. The invention is especially suitable for gas chromatograph separation column use.

To this date the analysis of the structure of phosphoric salts of group IV section A of the periodic chart and investigations into their natures has been carried out by most researchers from the standpoint of inorganic ion exchangers. The inventor and others have researched such inorganic ion exchangers in their catalyst function. Collaborating researchers have discovered that composition elements of metallic ions of Periodic Table groups I-III and VIII ion exchanged under certain conditions are beneficial to hydrolysis of halogenated aromatic hydrocarbons, or, for hydrocarbon state changes, beneficial to dehydrogenation, and so on, which has been granted patent Showa 40(1965)-80699. At this time, generally, the bigger the ratio area of the catalyst, the better the catalyst's activity. Further, to be able to make the ratio area

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\*Numbers in the margin indicate pagination in the foreign text.

change as required is even more desirable. However, the increase in ratio area will not fully come about merely as the result of pulverization.

When the inventor used inorganic ion exchangers as catalyst components, he discovered that the ratio area of the inorganic ion exchangers changed according to the differences in production methods used when the inorganic ion exchanger was produced. For example, it was discovered that composition elements obtained by washing and drying a precipitate obtained by forcing a reaction between phosphoric acid and Periodic Table group IV section A metallic salts in the mole ratios 0.6-1.7:1, and especially in the range of 0.9-1.5:1, without first heating it had very large ratio areas of 150 m<sup>2</sup>/g and above.

Measurements of the ratio area were made with the simple B.E.T. gas chromatograph method commonly in use, which was described by F.M. Nelsen and F.T. Eggertsen in Analytical Chemistry Vol.30, page 1387, 1958. The measurements were conducted at a temp of 300°C after one hour of drying.

In the following, in order to explain the invention and make the explanation easy to understand, the case in which phosphoric acid is used as the phosphoric acid base and Zirconium Oxychloride as the Periodic Table group IV section A metal will be used as an example.

Generally, a phosphoric acid Zirconium form ion exchanger can be obtained if a phosphoric acid solution is added to a solution of Zirconium Oxychloride dissolved in hydrochloric acid of strength 1 to 6. At such a time the ratio of the phosphoric acid base and Zirconium which reacts, when larger than a mole ratio of 0.5, can be changed over a wide range. However, until now, according to the reports we have seen, the mole ratio of the phosphoric acid base and Zirconium as the ion exchanger has generally been taken as 2.0. Consequently it has been generally thought that keeping the mole ratio of the phosphoric acid base and zirconium at the time of reaction near 2.0 is beneficial to production. Furthermore, once the precipitate

obtained in the reaction between Phosphoric acid and Zirconium Oxychloride has been filtered and the pH reaches 3-4 through thorough rinsing in water again after heating and drying, it is again dried to remove the hydrochloric acid and surplus acid. Generally the powder, especially if it is dried thoroughly, is produced as a 30-60 mesh large ion exchanger. In this case, to make the process of filtration easier it is usual to heat the precipitate before filtering to increase the size of the grains. /2

We also used the alternate method of first dissolving the Zirconium Oxychloride in a 6 strength concentrated hydrochloric acid solution to force the reaction thus obtaining a stable solution of dissolved Zirconium Oxychloride which makes the grains of the precipitate large enough to remove any difficulty from the filtration process. Nevertheless, comparing this method with making composition elements with large ratio areas and hitherto known results, in view of the remarkably large ratio area range, if we set as our purpose the ability to change the ratio area at will, there are many more conditions which must be established compared to commonly used methods.

The first of these consists of selecting a fixed value in the previous phosphoric acid base and Zirconium mole ratio of 0.6-1.7:1 (especially in the range of 0.9-1.5:1) in accordance with the surface product in mind and then mixing. Figure 1 shows just how much effect the relationship of the mole ratio between the phosphoric acid base and Zirconium has on the ratio area. This chart shows how the mole ratio ranges for the two components of 0.6-1.7, and especially 0.9-1.7, are suitable for obtaining the compositions from Phosphoric acid Zirconium with a ratio area higher than  $150\text{m}^2/\text{g}$  in the case where the mole ratio of the raw material components were changed under conditions the same as those shown in execution examples two and four. It also shows the generation of the desired ratio area as the mole ratio is changed inside the range of 0.6-1.7.

To continue on with the invention, regardless of what mole ratio

is chosen for the raw materials, the precipitate obtained at the time of reaction, that is, the composition ratio ( $\text{PO}_4/\text{Zr}$  mole ratio) of the final product, is always fixed, so the change in mole ratio merely affects the ratio area.

The next condition necessary for this method consists of washing the precipitate obtained in the reaction between Zirconium Oxychloride and the phosphoric acid base in water under almost normal temperatures until a pH of 3-4 is reached, and drying it after filtration is conducted. Consequently, as the washing must generally be conducted under conditions between normal and slightly raised temperatures, the high temperatures often used up to this point must be avoided. The effects of heating are especially remarkable when the operation is carried out while keeping the concentration of acid low. About the gas adsorption ability of the composition formed by Phosphoric acid Zirconium which can be said to be an effect of heat, it is primarily related to the ratio area, but when these compositions are used for, say, catalysts or carriers in the state change of propylene oxide, aside from the changes in ratio area that can be ascribed to heat, there is some affect on them as catalysts.

One other step which is necessary to obtain this kind of composition is to dehydrate the fine grind which has been washed and dried until the pH reaches 3-4 as described previously. Ordinarily the dehydration consists of heating at over  $100^\circ\text{C}$ . Figure 2 indicates the change in ratio area in the case of dehydration by means of heat of the composition obtained under the same conditions as execution example #5. It can be clearly seen from example #5 that high temperatures such as  $700^\circ\text{C}$  are not desirable for dehydration. Furthermore, there is a danger of causing a shift towards pyrophosphoric acid during the heating part of the process. The conditions of surface water absorption could be essential to the ratio area. If the dehydration is carried out completely in a vacuum and at temperatures of less than  $100^\circ\text{C}$ , then it is possible that dehydration can be performed at even lower temperatures.

For the purpose of producing compositions with large ratio areas, there is no need to use the customary technique of adding acid commonly used up till now when manufacturing ion exchangers; the acid may be either resent or lacking. However, from the standpoint of operation, the absence of acid facilitates rinsing.

The metals of Periodic Table group IV section A we use are Zirconium and Titanium. All of the water soluble configurations  $AX_4$ , (A is either Titanium or Zirconium; X is Chlorine, Bromine, or Iodine as the halogen. The following configurations use the same type of symbols.)  $AOX_2$ ,  $AOSO_4$ ,  $A(SO_4)_2 \cdot H_2O$ ,  $AO(OH)(NO_3)$ ,  $AO(NO_3)_2$ , and  $AO(OH)X$  are completely possible as choices for use.

Phosphoric acid was generally used as the phosphoric acid base to obtain these compositions, but phosphoric acid Titanium, phosphoric acid 2 Titanium, phosphoric acid 1 Potassium, and phosphoric acid 2 Potassium, etc., can all be used. However, it is not advisable to employ phosphoric acid alkali salts owing to the fact that the size of the grains becomes very small if the operation is carried out in the mole ratio range of 0.6-1.6, which results in some difficulty in keeping the formation conditions securely fixed.

As was previously written, this invention is an absorbent which employs as its main ingredient metallic salts of Periodic Table group IV section A with large ratio areas obtained through reaction between soluble metallic salts of Periodic Table group IV section A and a phosphoric acid base, the raw materials already mentioned. It is especially appropriate for use in gas chromatograph separator columns, and is not limited to production in the previously described manner.

#### Execution Example 1

55.6 g of 85 vol% phosphoric acid (specific gravity 1.70) is /3 diluted with 2.5ℓ of distilled water. A solution of 120g of  $ZrOCl_2 \cdot 8H_2O$  dissolved in 2.5ℓ of distilled water is added quickly while

stirring vigorously. At this point, the mole ratio of  $\text{PO}_4/\text{Zr}$  at preparation time is 13. Again, acid is not used in the  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  solution. After the white gel precipitate thus produced is left for 24 hours, 2ℓ of distilled water is added, it is decanted seven times, and when a pH of 3.5 is reached, it is filtered. After the precipitate (105g) is dried at  $110^\circ\text{C}$  for 24 hours it is pulverized. The grain size in each example is 30-50 mesh. (Note: for all execution examples dried for a full 24 hours at  $110^\circ\text{C}$  the grains were even and essentially did not need pulverizing. Ordinarily, if the drying was carried out at  $110^\circ\text{C}$  for a long time the grains were even within 30-60 mesh.) In accordance with usual practice the ratio area was measured after one hour of drying at  $300^\circ\text{C}$  and a figure of  $346 \text{ m}^2/\text{g}$  was attained.

#### Execution Example 2

120g of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  is dissolved in 2ℓ of distilled water. Meanwhile 37.2g, 55.6g, 68.7g, 81.6g, 94.4g, and 107.3g portions of 85 vol% phosphoric acid (specific gravity 1.70) are mixed with 1.9ℓ portions of distilled water. The two components are forced into reaction using a quantitative sending pump at a fixed speed to titrate for 3.4 hours approximately. The reaction tank is kept at  $40^\circ\text{C}$ . At this point, the  $\text{PO}_4/\text{Zr}$  mole ratios at the time of preparation are 1.0, 1.3, 1.6, 1.9, 2.2, and 2.5 respectively. The white gel precipitate, after being left for 24 hours, is filtered with 2ℓ of distilled water, 2ℓ of distilled water is added again and the filtration procedure is repeated 5 times. When the pH has reached 3.4, it is filtered out. The precipitate dries at a temperature of  $110^\circ\text{C}$  for 24 hours; from 102-106g of phosphoric acid Zirconium is obtained. The measured ratio areas after pulverization and one hour of drying at  $300^\circ\text{C}$  are, from the smallest mole ratio to the highest,  $273 \text{ m}^2/\text{g}$ ,  $325 \text{ m}^2/\text{g}$ ,  $176 \text{ m}^2/\text{g}$ ,  $15 \text{ m}^2/\text{g}$ ,  $12 \text{ m}^2/\text{g}$ , and  $14 \text{ m}^2/\text{g}$ . The result of composition analysis with fluorescent X-rays was, in all cases the fixed value of  $\text{PO}_4/\text{Zr}=1.0$ .

### Execution Example 3

120g of  $ZrOCl_2 \cdot 8H_2O$  are dissolved in 2.0ℓ of distilled water. A solution of 55.6g of 85 vol% phosphoric acid mixed into 2.0ℓ of distilled water is quickly added while stirring. The  $PO_4/Zr$  mole ratio at the time of preparation is 1.3. After the white gel precipitate thus created is left for 24 hours, 2ℓ of distilled water is added and the decanting procedure is repeated 9 times resulting in a pH of 3.4. The precipitate is filtered, then dried at  $110^\circ C$  for 24 hours. The ratio area after pulverization was  $340m^2/g$ .

### Execution Example 4

57.6g of tetrahedral Titanium salt is dissolved in 2ℓ of 1N - hydrochloric acid solution. Meanwhile, 57.6g, 75.09g, 92.3g, and 109.7g portions of 85 vol% phosphoric acid are each diluted with 1.9ℓ of distilled water. The two components are titrated for about 3.5 hours with a quantitative sending pump and mixed. The temperature of the mixing tank is kept at  $40^\circ C$ . This time, the  $PO_4/Ti$  mole ratios are, at the time of preparation, 1.0, 1.3, 1.6, and 1.9. The white gel precipitate thus formed is left for 24 hours and each sample is decanted seven times with 2.0ℓ of distilled water. When the pH=3.1-3.5 it is filtered. The precipitate obtained is dried at  $110^\circ C$  for eight hours then pulverized. As usual, the ratio area was measured and the following results were obtained. For P/Ti=1.0,  $258m^2/g$ ; for P/Ti=1.3,  $365m^2/g$ ; for P/Ti=1.6,  $80m^2/g$ ; and for P/Ti=1.9,  $9m^2/g$ .

### Execution Example 5

This shows the manufacturing conditions and analyzed values for phosphoric acid Zirconium gel.

Up till now the mole ratio for  $PO_4/Zr$  was kept at 2.0, but the result of our fluorescent X-ray analysis was a  $PO_4/Zr$  mole ratio of almost 1. However, the absolute value indicates that the  $PO_4/Zr$  mole

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ratio in the precipitates manufactured under any kind of conditions will be fixed.

Run. No.	(a) 調 製 条 件			(b) 生 成 物		
	塩酸濃度(N)	(c) P <sub>2</sub> O <sub>5</sub> /Zr のモル比	(d) 調製時間(h)	(e) 蛍光X線分析	比表面積 (m <sup>2</sup> /g)	(g)
1	1	0.9	0.5	0.95	290	
2	1	1.3	0.5	0.99	385	
3	1	2.2	0.5	0.98	12	
4	1	3.0	0.5	0.97	15	
5	1	6.0	0.5	0.96	8	
6*	5	3.0	72	0.97	16	
7	3	3.0	72	0.95	15	

Key: (a) Production conditions; (b) the formed object; (c) Hydrochloric acid concentration; (d) P/Zr mole ratio; (e) Preparation time (hrs); (f) Fluorescent X-ray analysis; (g) Ratio area (m<sup>2</sup>/g).

As the Zirconium Oxychloride recrystallizes if a hydrochloric acid solution of stronger than 6N is used, we employed hydrochloric acid of 5N and lower.

For the fluorescent X-ray analysis we used red phosphorus, the standard material for phosphorus analysis, and Zirconia, the standard material for Zirconium. The PO<sub>4</sub>/Zr mole ratio rather than the previously made test amount line was measured.

### Execution Example 6

74.9g of 85 vol% phosphoric acid (specific gravity of 1.70) are diluted in 2ℓ of distilled water. To this a solution of 133.6g of ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O is dissolved in 2ℓ of distilled water is quickly added while stirring. At this point the PO<sub>4</sub>/Zr mole ratio is 1.3. The white gel precipitate which is formed is left to sit for 24 hours, 2ℓ of distilled water is added, and the filtering procedure is performed five times. Nitric acid ions are removed and when the pH=3.3 then it is separated by filtration and dried for one day at 300<sup>0</sup>C, pulverized, then, after burning for one hour at 300<sup>0</sup>C, the ratio area is measured following normal procedure and the result of 297m<sup>2</sup>/g is obtained.

### Execution Example 7

Samples with a ratio area of  $236\text{m}^2/\text{g}$  produced with a  $\text{PO}_4/\text{Zr}$  mole ratio of 1.3 based on execution example 2 were ground in a pulverizing machine for over 16 hours. The ratio area was measured in the same way and a value of  $348\text{m}^2/\text{g}$  was obtained. Meanwhile, a sample produced with a  $\text{PO}_4/\text{Zr}$  mole ratio of 2.2 and a ratio area of  $12.0\text{m}^2/\text{g}$  before pulverization were similarly ground up in a pulverizer for more than 16 hours. The ratio area value of  $15.2\text{m}^2/\text{g}$  shown after pulverization was unassailable. If  $\text{PO}_4/\text{Zr}$  1.9 mole ratio samples with ratio area values of  $15.1\text{m}^2/\text{g}$  were subjected to this same procedure, then a ratio area value of  $18.1\text{m}^2/\text{g}$  value was consistently attained.

### Execution Example 8

Simultaneous analysis of carbon dioxide and carbon monoxide.

Metallic phosphoric acid salts with large ratio areas produced according to this method show interesting characteristics regarding adsorption. The adsorption ability for carbon monoxide and Olefin is extremely large. In order to clarify this, the examples when metallic phosphoric acid salts were used as filler for gas chromatograph use are shown below.

After the execution examples one through six are produced with grain sizes of 30-60 mesh or 60-80 mesh, they are plugged into a 1m long brass tube with an inside diameter of 6mm. Using this as a gas chromatograph separator column, the separating characteristics of organic and inorganic gases not easily condensed are checked using  $60\text{ml}/\text{min}$  of Helium as a carrier gas and changing the column temperature from room temperature to  $100^\circ\text{C}$ .

The result was, for any case using phosphoric acid Zirconium or phosphoric acid Titanium, if the phosphoric acid salts with large ratio areas are used, the separation characteristics of the various

gases are good, and the great adsorbency with regards to carbon monoxide and Olefin especially was confirmed.

An example of separation is given in the table below and in figure 4. The preservation time in seconds of each type of gas in regard to phosphoric Zirconium

Substance Name	Boiling Point (°C)	Column Temperature			
		15	32	60	100
CH <sub>4</sub>	-164	13	13	9	7
CO	-192	81	67	25	12
C <sub>2</sub> H <sub>6</sub>	- 93	83	59	29	16
CO <sub>2</sub>	- 78	325	175	67	41
C <sub>2</sub> H <sub>4</sub>	-103	-	343	175	103
C <sub>3</sub> H <sub>8</sub>	- 45	486	298	121	-

(|) When testing materials produced using a PO<sub>4</sub>/Zr mole ratio of 2 with very small ratio areas, the gases elute almost totally with air.

(||) When this method is used, especially separating carbon monoxide and Olefin from other manufactures, it can be eluted to any desired position.

#### Scope of the Patent Application

1 An adsorbent with its primary ingredient at least one metallic phosphoric acid salt constituting portion chosen from Zirconium and Titanium with large ratio areas.

Fig. 1

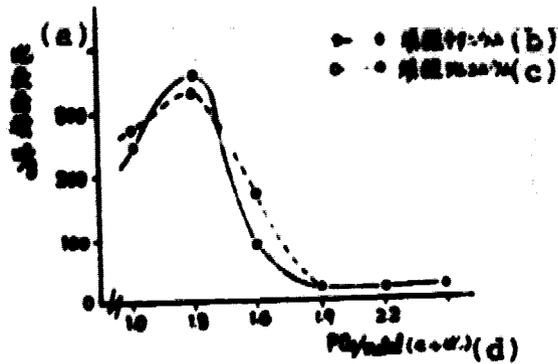


Fig. 2

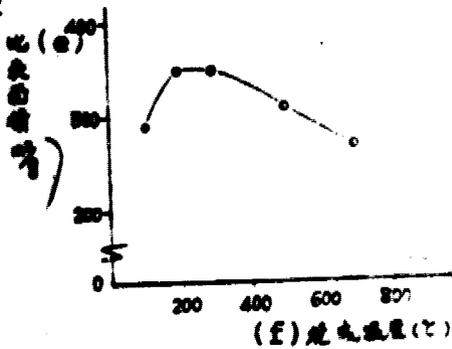
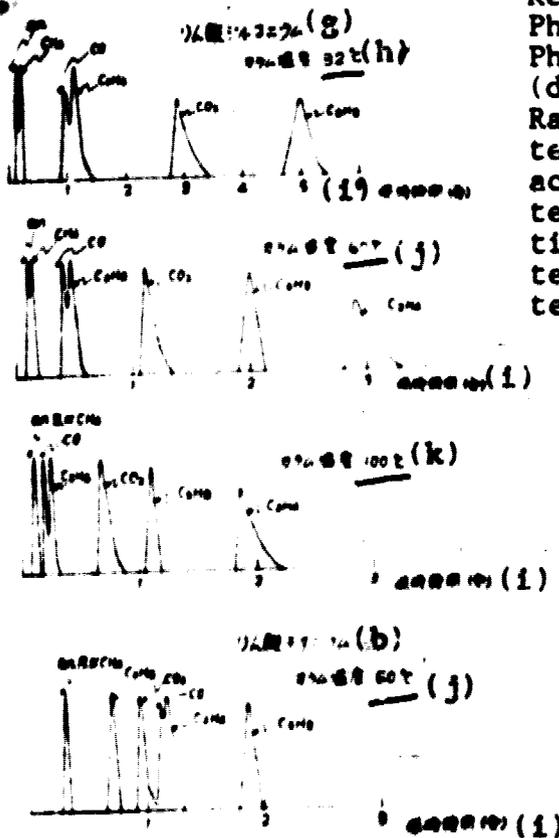


Fig. 3



Key: (a) Ratio area m<sup>2</sup>/g; (b) Phosphoric acid Titanium; (c) Phosphoric acid Zirconium; (d) PO<sub>4</sub>/metal mole ratio; (e) Ratio area m<sup>2</sup>/g; (f) Burning temperature; (g) Phosphoric acid Zirconium; (h) Column temperature; (i) Preservation time (minutes); (j) Column temperature 60°C; (k) Column temperature 100°C.