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# CATION-EXCHANGE PROPERTIES OF COPRECIPITATED SILICA-TITANIA GEL

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Silica-titania gel was found to be a polybasic acid and to exhibit ion-exchange abilities for alkali metal ions. In the chloride solutions, the ion-exchange reaction was relevant to ammonium and sodium ions on the gels, and in the hydroxide solutions, it also relevant to proton in addition to these two ions.

Silica-titania complex-oxide gel is a porous material stable at temperatures above 600°C 1) and shows distinguished solid acidity.2) We also found that this compound prepared by the homogeneous precipitation method was a good material for the adsorption of chromium (VI) ion from acidified solutions,3) the recovery of uranium in sea water,4) the color removal of dye solutions,5) etc. These findings have been assumed to be attributed to an ion-exchange reaction, because silica exhibited cation-exchange property,6) and titania both cation- and anion-exchange properties.7) To ascertain this assumption, we have preliminarily studied the ion-exchange properties of silica-titania gel for alkali metal ions.

A complex-oxide gel was precipitated from an equimolar mixture (0.2 mol $dm^{-3}$) of sodium metasilicate solution acidified with hydrochloric acid (pH 1) and titanium (IV) chloride by adding aqueous ammonia until pH 7 at 85°C. After aging for 10 h at 60°C, the resulting precipitate was filtered by suction, thoroughly washed with deionized water, and then dried at 110°C overnight. Grinding the dried gel, followed by granulation to the size of ca. 0.5 mm gave an ion-exchanger which included slightly sodium ion originated from one of the starting materials (sodium metasilicate) and ammonium ion arised from the precipitant (aqueous ammonia). A part of the ion-exchanger was subjected to the heat treatment at 700°C for 24 h in air. The uptake of alkali metal ions was examined in terms of a batchwise operation by shaking 0.2 g of ion-exchanger with 50 $cm^3$ of aqueous solution containing alkali metal ion to be studied (concentration of 0.01 mol $dm^{-3}$) for 24 h at 20°C. For a pH titration, the mixed solutions of sodium chloride and sodium hydroxide (both of 0.01 mol $dm^{-3}$) of various volume ratios were used. Alkali metal ions were determined by flame spectrophotometry and ammonium ion spectrophotometrically with the Nessler's reagent.8)

The pH titration curves were determined first in order to learn the acidic and basic properties of as-prepared and heat-treated silica-titania gels (Fig. 1).

The pH values of the solutions added with the gels were almost the same with those of the blank test in the lower pH range, but were brought down in the higher range. The phenomenon in the latter was probably resulted from the dissociation of surface protons on the gel and/or the dissolution of silica component (silicic acid) above pH 9.[9)] Further, both the curves changed abruptly at pH 7.4, as shown with zirconium (IV) phosphate[10)] and hydrous titanium (IV) oxide[11)] which possessed exchangable proton sites of different acid strengths. Therefore, the silica-titania gel seems to be similarly a polybasic acid.

Figure 2 shows the relationship between the apparent ion-exchange capacity of silica-titania gel and the equilibrium pH. The ion-exchange capacities for sodium ion of as-prepared and heat-treated silica-titania gels were 0.84 mequiv. $g^{-1}$ and 0.55 mequiv. $g^{-1}$, respectively. The difference between these capacities was detected only above pH 7.4, implying that the loss of the proton sites of lower acid strength by the heat treatment reduced their ion-exchange abilities. Also, these gels had the common tendency of an increase of ion-exchange capacity at three stages which could be separated at pH's 7.4 and 9.7. Particularly, the abrupt change at pH 7.4 with the heat-treated gel corresponded to the jump in the pH titration curve described above. From these three stages in Fig. 2, it was also proved that silica-titania gel was a polybasic acid with proton sites of different acid strengths.

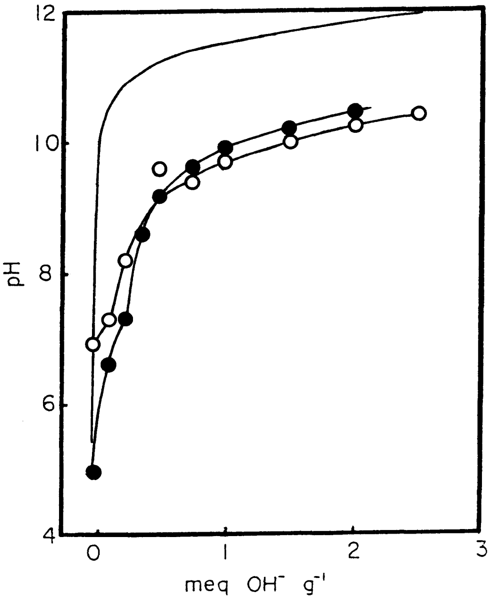

Fig. 1. Titration curves of silica-titania gels for sodium ion. -○- : as-prepared; -●- : heat-treated at 700°C for 2 h; —— : blank.

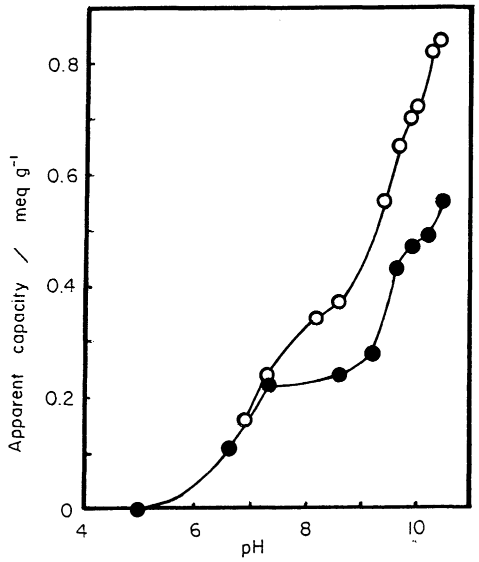

Fig. 2. Ion-exchange capacities of silica-titania gels for sodium ion as a function of pH. -○- : as-prepared; -●- : heat-treated at 700°C for 2 h.

Table 1. Effect of the complexing of silica and titania gels on the surface properties

| Gel[a)] | Uptake of ion[b)] mequiv. $g^{-1}$ Li | Na | K | Acid amount mmol $g^{-1}$ pKa≦+4.0 | Specific surface area $m^2 g^{-1}$ |
|---|---|---|---|---|---|
| Silica | 0.36 | 0.39 | 0.51 | 0 | 432 |
| Silica-titania | 0.81 | 0.84 | 1.06 | 1.73 | 264 |
| Titania | 0.97 | 0.74 | 0.61 | 1.19 | 228 |

a) As-prepared.
b) Hydroxide soln of 0.01 mol $dm^{-1}$.

The ion-exchange abilities of silica and titania gels for alkali metal ions except lithium were improved by the complexing of both gels, as can be seen in Table 1. It has been presumed on the formation and microstructure of silica-titania gel as follows: Acidified sodium metasilicate solution contains silica sol first which is converted to silica gel by the addition of aqueous ammonia after mixing with titanium (IV) chloride,[12)] titania gel also is precipitated from the mixed solution without too much delay,[13)] and then the resultant precipitate may be regarded as the intimate mixture of silica and titania gels in which the framework of silica gel is partly stuffed by widely spreaded titania gel, reducing the surface area of silica gel itself. It has also been probable that the occurrence of the bond, -Si-O-Ti-, around the interface of silica and titania particles caused the mixed gel to have a larger number of acidic sites than titania gel.

The determination of monovalent cations in aqueous solutions was carried out for the investigation of the stoichiometric relations as an ion-exchange reaction in the chloride solutions (Table 2). The uptake of alkali metal ion with silica-titania gel increased in the order of lithium, sodium, and potassium according to the increase in the ionic radius. The amount of cation liberated from the gel

Table 2. Ion-exchange of monovalent cations on silica-titania gel

| Solution[a)] | Uptake of $M^{+}$[b)] mequiv. $g^{-1}$ | Liberation of $NH_4^+$ mequiv. $g^{-1}$ | Liberation of $Na^+$ mequiv. $g^{-1}$ |
|---|---|---|---|
| LiCl | 0.18 | 0.14 | 0.06 |
| NaCl | 0.20 | 0.16 | — |
| KCl | 0.48 | 0.34 | 0.09 |
| LiOH | 0.79 | 0.19 | 0.02 |
| NaOH | 0.81 | 0.24 | — |
| KOH | 1.02 | 0.38 | 0.06 |

a) 0.01 mol $dm^{-3}$. b) $M^{+}= Li^{+}, Na^{+}$, or $K^{+}$.

into the solution was almost equal to that of alkali metal ion exchanged in an opposite direction. At this time, the pH value varied from 5.7 to 7, and then it seems reasonable to assume that the ion-exchange reaction proceeds as follows:

$$M^{+} \quad + \quad ST\text{-}NH_4^{+} \text{ (or -Na}^{+}) \quad \rightleftarrows \quad NH_4^{+} \text{ (or Na}^{+}) \quad + \quad ST\text{-}M^{+} \qquad (1)$$

where $M^{+}$ is alkali metal ion or proton and $ST\text{-}NH_4^{+}$ (or $-Na^{+}$) is ammonium ion (or sodium ion) located on the gel, respectively. The stoichiometric relations relevant to the ion-exchange reaction in the hydroxide solutions must also be realized, however, the amount of alkali metal ion uptaken was much more than the sum of the amounts of ammonium and sodium ions liberated, as shown in Table 2. At this time, the pH value fell from 12 to 11. It has, therefore, been considered that the reaction is further relevant to the exchangable proton sites on the gel in addition to Eq. 1, as given by Eq. 2.

$$M^{+} \quad + \quad ST\text{-}H^{+} \quad \rightleftarrows \quad H^{+} \quad + \quad ST\text{-}M^{+} \qquad (2)$$

Supposing the difference between the amounts of uptake and liberation for the alkali metal ions corresponds to that of proton related to the reaction, the stoichiometric relations which is called for as an ion-exchange reaction may be satisfied.

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