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Synthetic Inorganic Ion-Exchange Materials. LIV. The Amphoteric Behavior of Hydrous Titanium Dioxide Ion Exchangers in Different Preparations

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Hydrous titanium dioxides in amorphous form (Am-HTDO) were prepared in a state demineralized as much as possible through different processes. The equiadsorption point (EAP) for anion and cation was determined at an ionic strength of 0.1 with the use of alkali metal chloride solution. The EAP values were strongly affected by the synthetic method, especially hydrolysis pH, and by the kind of probing cations, ranging from 2.7 to 4.5. Chloride ion uptake was not dependent on the kind of coexisting cations. The EAP value of Am-HTDO prepared at pH>13 was appreciably lower than that of Am-HTDO prepared at pH 7—8. The "ion-free" Am-HTDO prepared by using the sol-gel method with $Ti[OCH(CH_3)_3]_4$ showed approximately the same EAP value as that of Am-HTDO hydrolysed at a similar pH by NaOH solution.

The zero point of charge (ZPC) has been widely used for describing the amphoteric nature of hydrous oxides and hydroxides.[1] They are defined by the pH value where the positive charge and negative charge are equal on the oxide surface, i.e., the overall surface charge density, σ_s, will be zero:

$$\sigma_s = F(z_+\Gamma_+ + z_-\Gamma_-)$$
$$\Gamma_+ = M_+/S_+,\quad \Gamma_- = M_-/S_-$$

where F is the Faraday constant; $z_+(z_-)$ the valence including sign; $\Gamma_+(\Gamma_-)$ the adsorption density of the ionic species; $S_+(S_-)$ the surface area available for cations or anions; and $M_+(M_-)$ the uptake of ions. The ZPC has been electrokinetically determined in the presence of a supporting electrolyte. Alkali metal chlorides are often used for ZPC determination: $z_+=z_-=1$. If the surface areas available for monovalent anions and cations are the same, equal uptake for each will give $\sigma_s=0$. Unfortunately the surface area available for anions and cations cannot be measured independently.

The ion-exchange process is implicitly involved in the preparation of hydroxides or hydrous oxides of multivalent metals through several routes. Alkali and alkaline earth cations are usually incorporated into the precipitate of metal hydroxides by ionic bonding. Often, they cannot be removed by washing with water alone. When the material contains exchangeable components such as Na^+ and Cl^- and complexing organic ions such as acetate and oxalate, the involved process (1) and/or (2) will not allow the determination of the intrinsic ZPC of the pure material without ionic impurities.

$$\equiv M\text{-}O^-B^+ + H_2O \rightleftarrows \equiv M\text{-}OH + BOH \tag{1}$$
$$\equiv M\text{-}OH_2^+X^- + H_2O \rightleftarrows \equiv M\text{-}OH + H_3O^+ + X^- \tag{2}$$

or

$$\equiv M\text{-}X + 2H_2O \rightleftarrows \equiv M\text{-}OH + H_3O^+ + X^- \tag{3}$$

where M denotes the central metal ion. Accordingly, the presence of exchangeable cationic impurity will shift the ZPC to a larger value, while the presence of the anionic impurity will shift the ZPC to a smaller value. Little attention has hitherto been paid to those exchangeable components by other authors.

It was difficult to remove K^+ completely in a cryptomelane-type hydrous manganese dioxide (CRYMO) because of an extremely high selectivity even though concentrated nitric acid was used as the conditioning solution. The CRYMO in the 'H^+ form' still contained 0.06 mequiv K^+/g. Its ZPC was estimated to be smaller than 2,[2] while Healy et al.[3] reported a value of 4.5±0.5. They used a synthetic cryptomelane containing a considerable amount of K^+ ions. The surface area, determined by the N_2 adsorption method, was employed for the determination of the charge density on the ionogenic surface. The surface area strongly depends on the crystal structure, and on the amounts of ions incorporated into a solid which often clog the ion channel and produce a much smaller surface area.[4] Hence, it is a primary consideration to remove exchangeable ionic impurities as completely as possible and to determine the surface areas S_+ and S_- for the evaluation of the intrinsic ZPC. However, it is not easy to measure each surface area, because the N_2 molecule and the exchanging ions have different dimensions. It is often assumed that $S_+=S_-$ to locate the ZPC.

The nature of hydrous oxides of multivalent metals can be well specified by a new concept of the equiadsorption point (EAP).[5] It was introduced as an acid-strength parameter and defined as the pH where the equivalent uptake of K^+ and Cl^- takes place:

$$[\equiv M\text{-}O^-K^+] = [\equiv M\text{-}OH_2^+Cl^-] \quad (\text{mequiv g}^{-1})$$

The ion-exchange processes have been clearly defined by the above Eqs. 1 and 2 on the various hydrous oxides.[6-8] When $S_+=S_-$ and $z_+=z_-$, the ZPC will be equal to the EAP. The EAP value is a more direct parameter than the ZPC as the index of the amphoteric nature of the oxides or hydroxides. The ionic

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potential (Z/r) has been found to be the principal parameter for the determination of the EAP for MO_2-type oxides.[9] Z and r denote the formal charge and the cystal ionic radius[10] of the metal ion, M^{Z+}. The EAP is parallel with the ionic potential sequence:

$$SiO_2 < MnO_2 < TiO_2 < SnO_2 < ZrO_2 < CeO_2 < ThO_2$$

A similar order in the ZPC value has been found by Ahmed and Maksimov.[11,12]

Nevertheless, a large discrepancy can be found among the EAP values reported for hydrous titanium dioxides. There have been several types of hydrous titanium dioxides known as the ion exchanger: amorphous, anatase- and rutile-types[9] and layered titanic acids.[13,14] A reported EAP is 3.4 for amorphous titanium dioxide and 4.5 for anatase-type hydrous titanium dioxide.[15] It may be due to the degree of crystallization, modification, possibly contamination, and other factors.

The present paper describes the 'intrinsic' EAP of hydrous titanium dioxides of amorphous type.

Experimental

Preparation of Amorphous Hydrous Titanium Dioxide (Am-HTDO). A-1: A 70 g aliquot of titanium tetraisopropoxide $Ti[OCH(CH_3)_2]_4$ (TTP) was hydrolyzed by adding it dropwise into demineralized water (750 cm^3) at 5 °C with mild stirring. The precipitate was aged at 5 °C for 3 d, washed thoroughly with water centrifuged at 13000 rpm and air-dried at room temperature. The dried material was ground and sieved into 100—200 mesh size. The adhering fine particles were removed by washing before use.

A-2: TTP/cyclohexane solution (40 g of TTP/520 cm^3 cyclohexane) cooled at 10 °C was floated on water (430 cm^3) at the same temperature. A precipitate was allowed to form in the interface of cyclohexane and water. The precipitation rate was slower than by method A-1. The precipitate was washed in the similar manner as A-1 and dried at 85 °C.

A-3: A 70 g aliquot of TTP solution was hydrolyzed by adding slowly to an 820 cm^3 of 1.8 M (M=mol dm^{-3}) NaOH solution at 5 °C. The precipitate was aged for one week, and then excess NaOH and isopropyl alcohol were removed by washing. The dried semitransparent material was ground, sieved into 100—200 mesh size and conditioned into the H^+ form with the column method by using 0.02 M HNO_3 solution.

B-1: This was prepared by the method reported previously.[15] A 50 cm^3 aliquot of $TiCl_4$ was preliminarily hydrolyzed by adding 150 cm^3 of water, followed by precipitation with a slow addition of 800 cm^3 of 2.8 M NaOH solution. The precipitate was washed repeatedly, percolated with a filter paper and air-dried. The conditioning procedure was the same as for A-3.

B-2: A precipitate was prepared by adding 2.8 M NaOH solution to the prehydrolyzed $TiCl_4$ aqueous solution until pH 7—8. The subsequent procedure was the same as for B-1.

Materials Characterization. Sodium and Ti were determined by atomic absorption spectrometry and inductively coupled plasma (ICP) emission spectrometry (SEIKO, Model SPS 7000), respectively. Nitrate ion was determined spectrophotometrically by the brucine method.[16] Powder X-ray diffraction analysis was carried out using Cu $K\alpha$ radiation with a JEOL Model JDX-7E X-ray diffractometer. Thermal analyses (TG and DTA) were undertaken with a Rigaku Denki thermoflex-type thermal analyzer, Model 8076 at a heating rate of 10 °C min^{-1} by using α-Al_2O_3 as the reference material. Infrared spectra were measured with the KBr disk method by using a JEOL spectrometer, Model DS-701G.

Ion-Exchange Study. A 20 cm^3 aliquot of 0.1 M (MCl+MOH or HCl) (M=Li, Na, or K) was added to an 0.200 g portion of the H^+ form sample. After 7 d equilibration, pH and concentrations of metal ions and Cl^- were analyzed for the liquid phase. Ion uptake was determined from the difference relative to the initial concentration.

Reagents. All the chemicals used were supplied by Wako Pure Chemical Ind., Ltd. These were of reagent grade.

Results and Discussion

Ion-Exchange Materials. All the products in the H^+ form were amorphous except the sample A-2 with a weak (101) reflection, indicating it to be weakly crystallized (Fig. 1, left). The endothermic peak was observed at 100 °C for the sample A-2 and at 130 °C for the others (Fig. 2). The exothermic peak appeared at 400 °C for the samples A-3 and B-1 prepared by addition of NaOH upto pH>13. A-1 and weakly crystallized A-2 showed the exothermic peak at 350 and 320 °C respectively. These exothermic peaks were assigned to the crystallization to anatase-type hydrous titanium dioxide, which was indicated by the X-ray pattern (Fig. 1, right).

The large IR absorption peak at 3500—2900 cm^{-1} can be assigned to the stretching mode and the absorption band at 1630 cm^{-1} to the bending mode of water adsorbed on the solid (Fig. 3). Absorption bands were observed at 1530 and 1330 cm^{-1} in the sample B-1 before conditioning with 0.1 M HNO_3 solution. These could be assigned to the symmetric mode and the asymmetric mode of the CO_3^{2-} adsorbed.[17] There was no absorption band between 2960—2850 cm^{-1} characteristic for isopropyl alcohol and cyclohexane. Hence, these organics could be completely removed by washing with H_2O and/or conditioning with 0.1 M HNO_3 solution. The chemical composition of these samples is given in Table 1 along with the synthetic conditions.

EAP Values. Hydrous titanium dioxides (A-1) indicated the amphoteric nature (Fig. 4). At lower pH than 4, they indicated a monoacidic base and at higher pH than 4 they indicated a dibasic acid. The difference between the blank and the titration curve should give the apparent capacity at the specified pH value if the ion-exchange process is predominant. Actually the uptakes determined for each ion agreed well with the calculated uptake from the titration curve in the pH range studied. Accordingly, the

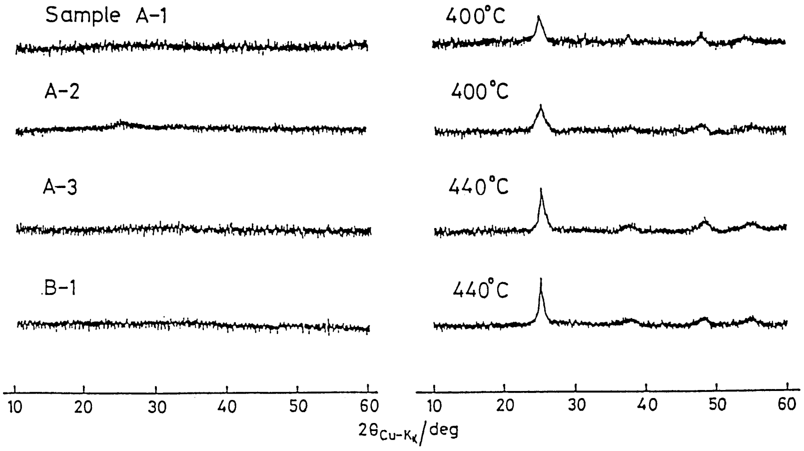

Fig. 1. Powder X-ray diffraction patterns of hydrous titanium dioxides prepared at various conditions. Left: as prepared in H^+ form, Right: sample heated upto the temperature indicated, where the exothermic peak ends.

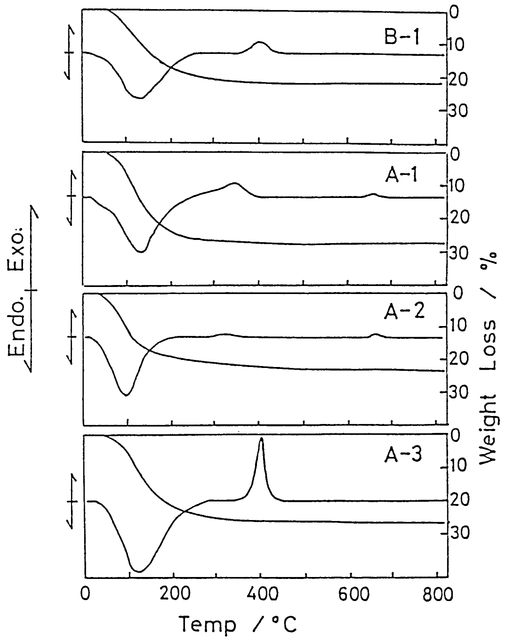

Fig. 2. TG and DTA curves of hydrous titanium dioxides. Heating rate: 10 °C min^{-1}.

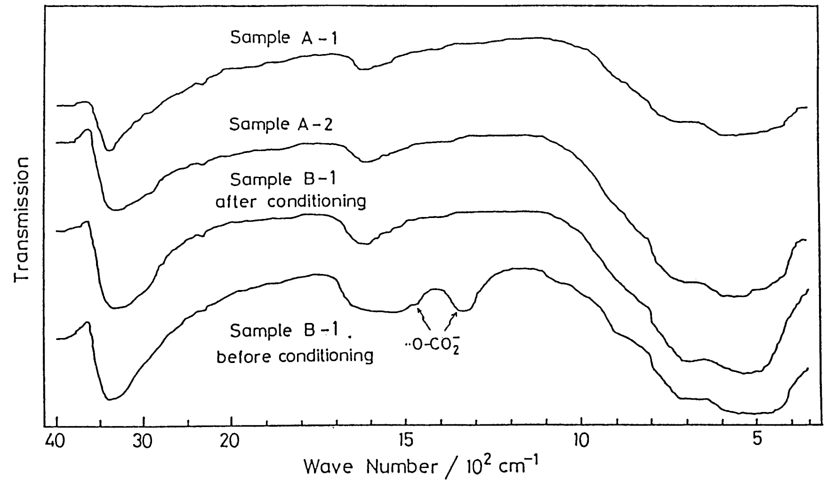

Fig. 3. Infrared spectra of various hydrous titanium dioxides.

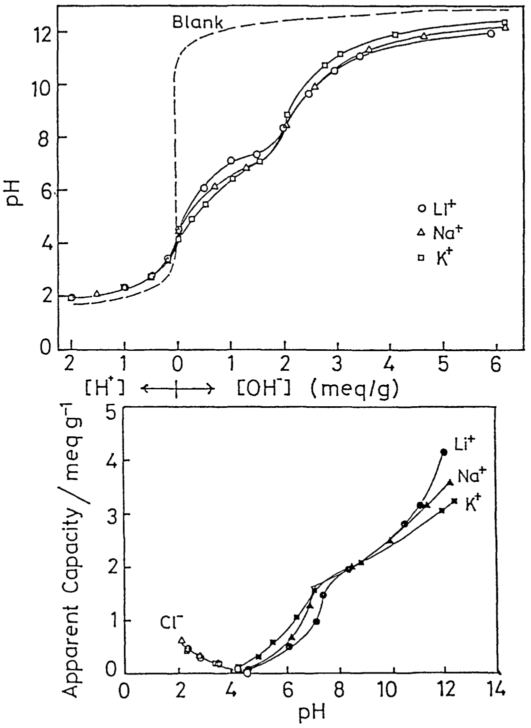

Fig. 4. pH titration curves (top) and apparent capacities (bottom) of sample A-1. HTDO: 0.20 g, soln: 0.1 M (MCl+HCl or MOH), total vol.: 20 cm^3, temp: 30 °C.

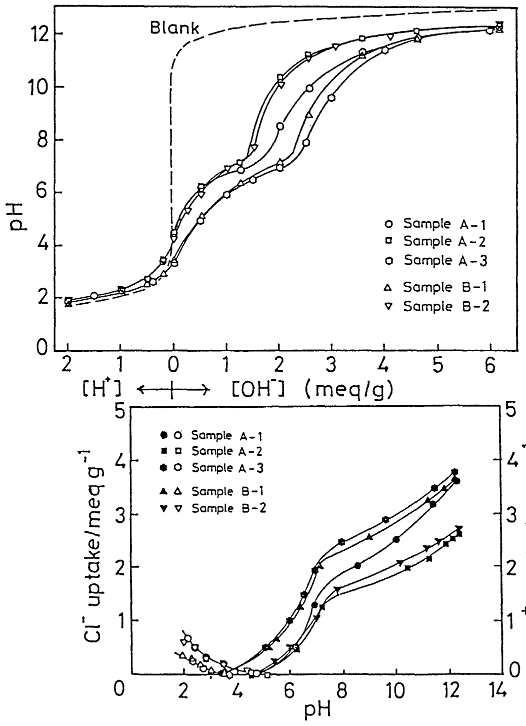

Fig. 6. pH titration curves (top) and apparent capacities (bottom) of HTDO prepared at different conditions. The conditions of measurement are the same as Fig. 4.

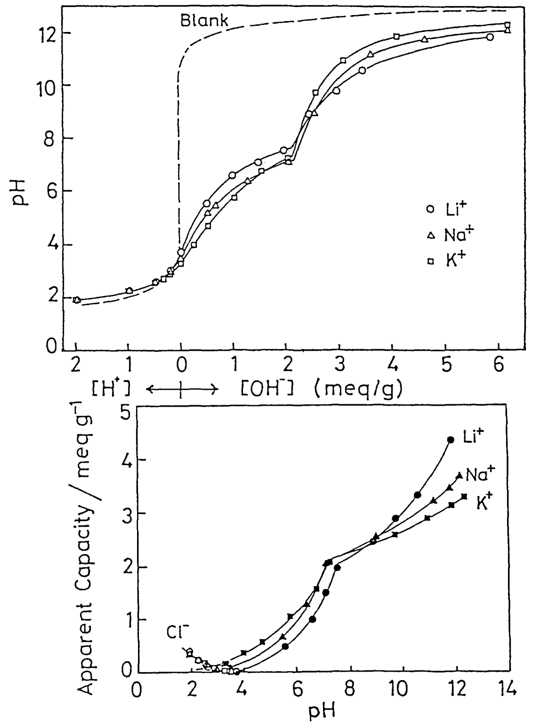

Fig. 5. pH titration curves (top) and apparent capacities (bottom) of sample B-1. The conditions of measurement are the same as Fig. 4.

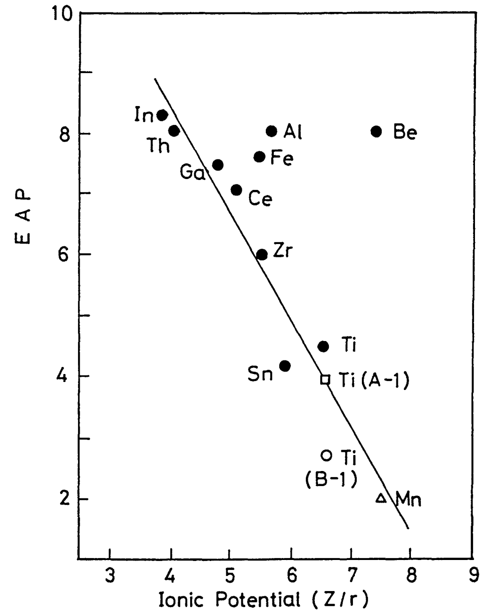

Fig. 7. Linear correlation between the ionic potential and the EAP value of hydrous oxides of multivalent metals. Exchanging ions: K$^+$, Cl$^-$. Ionic strength: 0.1, ● Ref. 5, □: TiO$_2$(A-1), ○: TiO$_2$(B-1), △: MnO$_2$ from Ref. 2.

Table 1. Synthetic Conditions, Chemical Compositions, and EAP of Hydrous Titanium Dioxides for Different Preparations

Sample	Starting materials	Hydrolysis temp and pH	Drying temp	XRD	Chemical composition (impurities)	Exchanging ions	EAP
A-1	TTP 70 g + H_2O 750 cm^3	5 °C, pH 7	20 °C	Amorphous	$TiO_2 \cdot 1.68H_2O$ (free from ions)	Li, Cl Na, Cl K, Cl	4.5 4.4 4.0
A-2	TTP/cyclohexane (40 g/520 cm^3) + H_2O 430 cm^3	10 °C, pH 7	85 °C	Very weakly crystallized to anatase-type	$TiO_2 \cdot 1.36H_2O$ (free from ions)	Na, Cl	4.4
A-3	TTP 70 g + 2.8M NaOH 820 cm^3	5 °C, pH>13	20 °C	Amorphous	$TiO_2 \cdot 1.68H_2O$ (Cl^-, NO_3^- <DL[a])	Li, Cl	3.6
B-1	$TiCl_4$ 50 cm^3 +H_2O 150 cm^3 +2.8M NaOH 800 cm^3	20 °C, pH>13	20 °C	Amorphous	$TiO_2 \cdot 1.25H_2O$ (Na^+ 0.045 mequiv g^{-1}; Cl^-, NO_3^- <DL[a])	Li, Cl Na, Cl K, Cl	3.6 3.3 2.7
B-2	$TiCl_4$ 50 cm^3 + H_2O 150 cm^3 +2.8M NaOH	20 °C, pH 7—8	20 °C	Amorphous	$TiO_2 \cdot 1.14H_2O$ (Cl^-, NO_3^- <DL[a]; Na^+ 0.045 mequiv g^{-1})	Na, Cl	4.4

a) DL=detection limit. DL for Cl^-: 0.001 mequiv g^{-1}, NO_3^-: 0.005 mequiv g^{-1}.

uptake of alkali metal ions and Cl^- with A-1 prepared by the sol-gel procedure was due to the ion-exchange process. The apparent capacity of the cation increased in the order: $Li^+ < Na^+ < K^+$ at $pH < 7.5$ and $K^+ < Na^+ < Li^+$ at $pH > 10$. The reversal of the capacity will be due to the steric hindrance coming from the crystal ionic radius of exchanging ions and the limited space of the exchange sites. The small Li^+ can go into the small ion-exchange cavity while the large K^+ cannot access the cavity. The Cl^- uptake was not dependent on the variety of the co-existing cation. The EAP determined was 4.5, 4.4, and 4.0 for LiCl, NaCl, and KCl systems, respectively.

The titration curve of the sample B-1 gave the small EAP values: 2.7 for KCl system, 3.3 for NaCl system and 3.6 for LiCl system (Fig. 5). These data are in good agreement with those reported previously.[15,18] The values are smaller than those for the sample A-1. If the sample contains exchangeable components, the EAP value will be shifted to larger or smaller values, as mentioned above, according to the Eq. 1 or 2. Chemical analysis showed an exchangeable impurity of 0.045 mequiv g^{-1} for Na^+ and <0.005 mequiv g^{-1} for NO_3^-. Therefore, the effect by the process (1) will be larger than by the process (2). It means that the EAP value of the sample B-1 should become higher than that of the sample A-1 containing negligible amounts of ionic impurities. Accordingly, the lower EAP value cannot be ascribed to these ionic impurities of the sample B-1. The EAP values were compared for the samples prepared under different conditions (Fig. 6). Am-HTDOs prepared at pH 7 showed a higher EAP than those prepared at high pH (>13) using the same starting material. More acidic ion-exchange sites are formed over a high pH region. The starting materials did not substantially affect the EAP.

The EAP values determined for the Am-HTDOs are summarized in Table 1. They were found to vary depending on the exchanging ions used and the pH on hydrolysis even though the ionic impurities were lowered to a negligible level. Some selected EAP values were plotted against the ionic potential (Z/r) along with the EAP value for a cryptomelane-type hydrous manganese dioxide (Fig. 7). The latter value was taken from the reference.[2] These EAP values for various HTDO fall on a straight line and ranged from 2.7 to 4.5. The results indicate the importance of hydrolysis pH in the preparation of HTDO and the complete removal of exchangeable ionic impurities.

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