

A New Layered Hydrous Titanium Dioxide $H_xTi_{2-x/4}O_4 \cdot H_2O$

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Interlayer caesium ions are extracted in a topotactic manner from $Cs_xTi_{2-x/4}O_4$, giving rise to a new layered hydrous titanium dioxide, $H_xTi_{2-x/4}O_4 \cdot H_2O$, with large interlayer spacing and low charge density of the host layer.

A few types of layered hydrous titanium dioxide, e.g. $H_2Ti_3O_7$,¹ $H_2Ti_4O_9 \cdot nH_2O$,^{2,3} have been reported so far. Their prominent intercalation abilities have given promising prospects for sorption, separation, treatment of radioactive wastes and catalysis.⁴⁻⁷ The abilities are generally dependent on a number of factors such as composition, crystal structure, layer charge and so on. We now report the synthesis of a novel layered hydrous titanium dioxide characterized by its smooth surface and low charge density of host framework.

Grey *et al.* have reported the preparation and crystal structure of a nonstoichiometric caesium titanate $Cs_xTi_{2-x/4}O_4$.^{8,9} The titanate has an orthorhombic layer structure in which two-dimensional macroanions of $[Ti_{2-x/4}O_4]^{x-}$ hold charge-balancing Cs ions between them. The macroanion has a relatively smooth surface compared with the corrugated ones for $[Ti_3O_7]^{2-}$ and $[Ti_4O_{10}]^{2-}$ by being stepped every three and four octahedra, respectively. In this study, we attempted to extract Cs ions from $Cs_xTi_{2-x/4}O_4$ by the action of aqueous HCl in order to transform it to a layered hydrous titanium dioxide.

The caesium titanate $Cs_xTi_{2-x/4}O_4$ was prepared by calcining a mixture of TiO_2 and Cs_2CO_3 at 1073 K. After two sets of calcination for 20 h, resulting phases were identified by powder X-ray diffraction (XRD). A homogeneous single phase of $Cs_xTi_{2-x/4}O_4$ was obtained with a starting molar ratio of TiO_2 to Cs_2CO_3 from 5.0–5.5:1. The nonstoichiometric parameter, x , ranges from 0.67 to 0.73. The Cs extraction was carried out by treating 10 g of $Cs_xTi_{2-x/4}O_4$ with 1 dm³ of aqueous HCl (concentration: 1 mol dm⁻³) at room temperature for 3 days. The solution was replaced with a fresh one every 24 h.

The chemical analysis found 2.3 wt% for Cs_2O , 81.7 wt% for TiO_2 and 16.2 wt% for H_2O for the HCl-treated product ($x = 0.70$). This means the achievement of almost full (~98%) extraction of Cs ions.

Fig. 1 shows the XRD patterns for the material ($x = 0.70$) before and after the HCl-treatment. Body-centred ortho-

rhombic symmetry was maintained after the treatment. The refined lattice parameters were $a = 3.837(1)$, $b = 17.198(3)$, $c = 2.960(1)$ Å for $Cs_xTi_{2-x/4}O_4$ ($x = 0.70$) and $a = 3.783(2)$, $b = 18.735(8)$, $c = 2.978(2)$ Å for its HCl-treated material. It is

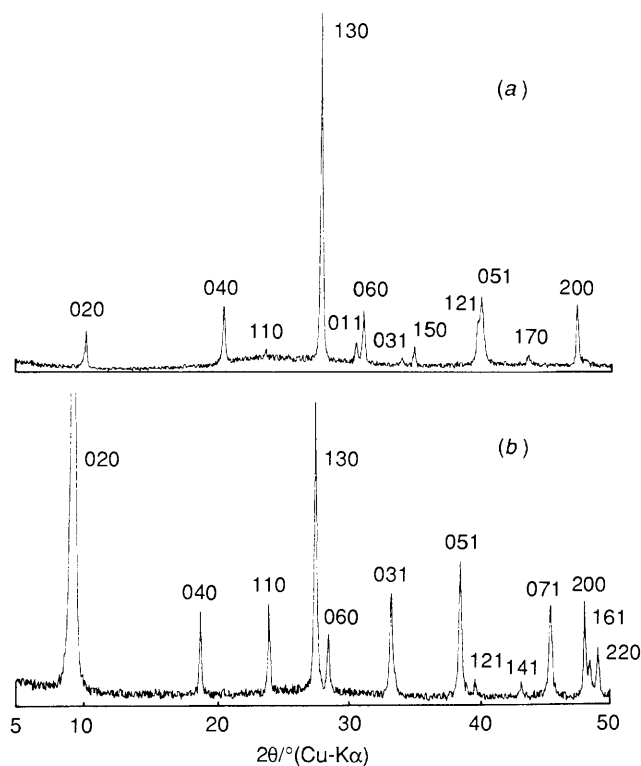


Fig. 1 Powder X-ray diffraction patterns (a) $Cs_xTi_{2-x/4}O_4$ ($x = 0.70$), (b) HCl-treated product

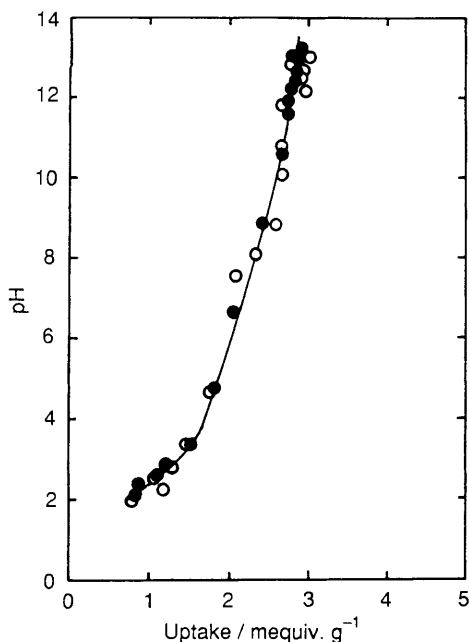
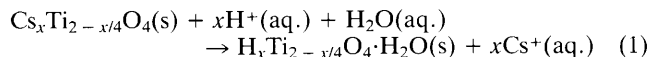


Fig. 2 pH Titration curves ●: K, ○: Cs; solid: $H_xTi_{2-x/4}O_4 \cdot H_2O$, 0.2 g; titrant: 0.1 mol dm⁻³ (MCl-MOH) solution, 20 cm³, M = K, Cs

evident that the host framework was not destroyed by the Cs extraction.

A new type of layered hydrous titanium dioxide has thus been obtained in a topotactic manner as given in eqn. (1). The water content was approximately unity per formula weight, not being dependent on x . The IR spectrum showed two broad bands at 3400 and 1640 cm⁻¹, which may be assigned to stretching and bending vibrations of H₂O and/or H₃O⁺, respectively. An absorption band at 960 cm⁻¹, characteristic of the bending mode of hydroxyls in hydrous titanates, was not detected. The data suggest that the material contains exchangeable protons as interlayer oxonium ions, not as hydroxyl groups.



The interlayer distance ($b/2 = 9.4 \text{ \AA}$) and the free area per unit layer charge ($2ac/x = 30.7\text{--}33.6 \text{ \AA}^2$), the reciprocal of the charge density, for $H_xTi_{2-x/4}O_4 \cdot H_2O$, are larger than those for the other types of layered hydrous titanium dioxide: H₂Ti₃O₇: 7.9 Å, 17.2 Å²; H₂Ti₄O₉· n H₂O: 9.1 Å; 22.5 Å². It is expected that $H_xTi_{2-x/4}O_4 \cdot H_2O$ can accommodate rather large cations and molecules with less steric hindrance. The charge density is one of the lowest among lamellar inorganic compounds, with the exception of smectite clay minerals.

Acid-base properties were examined (Fig. 2) by titrating the material with aqueous KOH and CsOH. There was no appreciable difference in the incorporation behaviours of the two cations; about 1 mequiv. g⁻¹ of uptake was observed around pH 2, which reached almost 3 mequiv. g⁻¹ at pH 12 and above. The interlayer distance shrank continuously as the cation loading increased. This fact as well as the absence of features in the titration curves indicates that the cations incorporated are forming a solid solution. This behaviour contrasts with that for H₂Ti₃O₇ and H₂Ti₄O₉· n H₂O; the latter two exhibit stepwise intercalation processes accompanying discontinuous changes in interlayer distance, which are distinctive for each cation or molecule incorporated.³⁻⁷

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