Preparation of Silica-pillared Layered Tetratitanate with a High Surface Area

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A novel pillaring procedure was developed to prepare the first example of silica-pillared layered tetratitanate; the resultant pillared material is porous, with a high surface area of 184.5 $m^2 g^{-1}$ and retaining thermal stability to above 550 °C.

Insertion of large inorganic polyoxo cations into water-swellable smectite clays can produce expanded porous materials. Such 'pillaring' of layered aluminosilicates has given rise to many attempts to prepare new high surface area materials which can be used as shape-selective catalysts and molecular sieves.[1,2] There are also a wide variety of layered metal oxides that have the potential to undergo ion-exchange reactions analogous to those observed with clays,[3–5] but the pillaring procedures developed for smectite clays are not generally applicable to these laminar metal oxides that do not spontaneously delaminate in aqueous media due to their high charge densities on the frameworks, although the direct reaction of a layered sodium trititanate with an aluminium oligomeric cation has recently been noted.[6] Using a stepwise exchange procedure, Cheng and Wang[7] have prepared alumina-pillared layered tetratitanates. We have reported that layered niobate and titanoniobate can react with $NH_2(CH_2)_3Si(OEt)_3$ (APS) in aqueous solution to form porous, thermostable silica-pillared layered metal oxides.[8,9] However, contrary to layered niobate and titanoniobate, layered $H_2Ti_4O_9{\cdot}nH_2O$ can not be treated in a similar way to obtain silica-pillared layered tetratitanate due to its relatively low acidity.[4] Large-size APS oligomers formed by hydrolysis and polymerisation in aqueous solution[10,11] generally prevent the facile intercalation of APS into layered tetratitanate. We now report the preparation of silica-pillared layered tetratitanate by a novel pillaring procedure. It entails first intercalating layered tetratitanate with *n*-hexylamine and then treating the *n*-hexylamine-intercalated tetratitanate with an aqueous solution of APS, and finally calcining the solid product in air to remove the interlayer organics. The resultant silica-pillared layered tetratitanate is porous, and has a high surface area of 184.5 mg g^{-1} and shows thermal stability at temperatures >550 °C.

Layered tetratitanate ($K_2Ti_4O_9$) was prepared according to the literature procedure.[3] Ion exchange of $K_2Ti_4O_9$ was carried out with 1 mol dm^{-3} HCl at 70 °C for 6 h to afford $H_2Ti_4O_9{\cdot}nH_2O$. *n*-Hexylamine-intercalated tetratitanate was obtained by adding $H_2Ti_4O_9{\cdot}nH_2O$ (10 g) to a 50% *n*-hexylamine–ethanol solution (100 ml) and stirring at room temperature for 3 weeks, followed by centrifugation and washing successively with ethanol–water (1:1) and distilled water. *n*-Hexylamine-intercalated tetratitanate (5.0 g) was then refluxed with an aqueous solution (10 wt% APS 500 g) under stirring for 84 h. After reaction, the solid product was separated by centrifugation and washing as above and finally dried at 50 °C.

Although $H_2Ti_4O_9{\cdot}nH_2O$ cannot react directly with an aqueous solution of APS to form an intercalate, *n*-hexylamine readily intercalates layered tetratitanate and increases the interlayer distance to 21.6 Å ($2\theta = 4.1°$) [Fig. 1(*a*)]. The peaks at 2θ 4.1, 8.2 and 12.3° are indexed to the (001), (002) and (003) planes, respectively. The *n*-hexylamine-intercalated tetratitanate has a rather low thermal stability, and collapses after heating to 450 °C [Fig. 1(*b*)]. However, the opened layers of *n*-hexylamine-intercalated tetratitanate can facilitate the reaction of layered tetratitanate with APS in aqueous solution. As shown in Fig. 1(*c*), two (001) diffraction peaks can be observed upon treatment of *n*-hexylamine-intercalated tetratitanate with an aqueous solution of APS. One of these ($2\theta = 4.0°$) is attributed to layered tetratitanate intercalated by APS oligomers formed in aqueous solution while the other ($2\theta = 4.5°$) arises from residual *n*-hexylamine-intercalated tetratitanate. A shift in 2θ from 4.1 to 4.5° is due to the fact that some of *n*-hexylammonium ions within the layers are lost during the reaction. Acid-base and ion-exchange reactions are responsible for the partial displacement of *n*-hexylammonium ions and the entrance of APS oligomers into the opened tetratitanate layers. According to ^{29}Si MAS NMR, the main APS oligomers within the layers are tri- and di-meric silicate species.[12] TGA and DTA of this reaction product show that the interlayer organics begin to decompose at 315 °C. Therefore, calcining in air leads to the decomposition of interlayer organics, and silica-like clusters are formed *in situ* within the layers[12] which act as pillars to prop up the tetratitanate layers, *i.e.* a silica-pillared layered tetratitanate is obtained. This has an interlayer distance of 13.4 Å ($2\theta = 6.6°$) and retains thermal stability to >550 °C [Fig. 1(*d*)]. The interlayer spacing of 13.4 Å collapses upon heating to 650 °C [Fig. 1(*e*)]. Elemental analysis results show that the SiO_2 content in this silica-pillared material is 87.2 wt %.

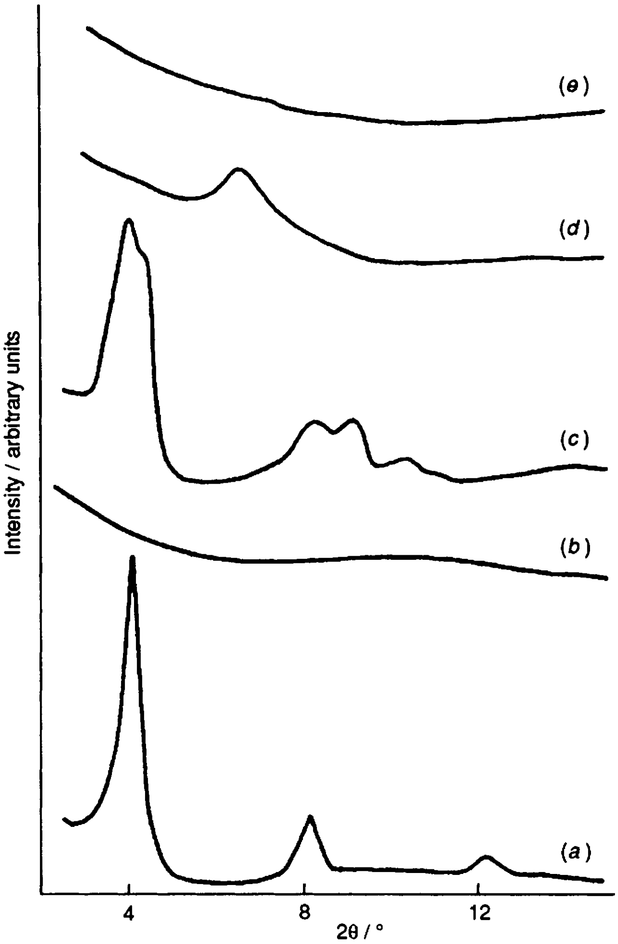

Fig. 1 Cu-Kα X-ray diffraction patterns of (*a*) *n*-hexylamine-intercalated tetratitanate; (*b*) as (*a*), calcined in air at 450 °C for 2 h: (*c*) reaction product of *n*-hexylamine-intercalated tetratitanate with an aqueous solution of APS; (*d*) as (*c*), first calcined in air at 450 °C for 2 h and then at 550 °C for 2 h, and (*e*) as (*d*), calcined in air at 650 °C for 2 h

The porosity of this silica-pillared layered tetratitanate is examined in terms of N_2 adsorption–desorption isotherms and is shown in Fig. 2. The hysteresis of the curve demonstrates that the silica-pillared layered tetratitanate is porous. The pore-size distribution analysis results show that both micro- and meso-pores are present, with an average pore diameter of 30.8 Å. *n*-Hexylamine intercalated tetratitanate decomposed at the same outgassing conditions (350 °C, 0.26 Pa, 4 h) as evidenced by XRD and IR.

The surface area of the starting material ($K_2Ti_4O_9$) is very low (3.3 $m^2 g^{-1}$). By comparison, the silica-pillared layered tetratitanate has a much higher surface area of 184.5 $m^2 g^{-1}$, indicative of an appreciable intracrystal surface area suitable for molecular adsorption and shape-selective catalysis.

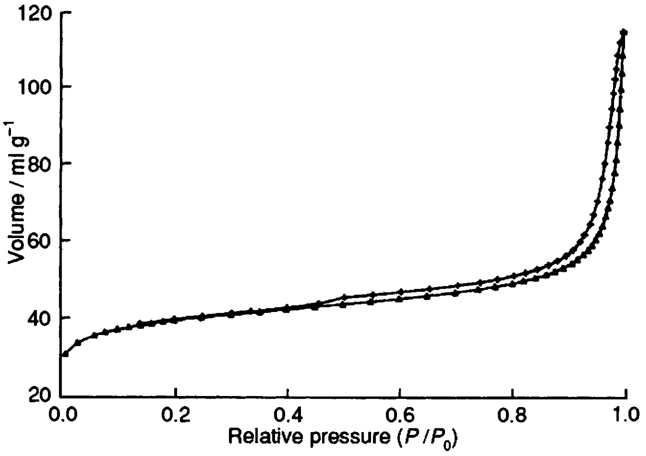

Fig. 2 Adsorption–desorption isotherm of N_2 on the silica-pillared layered tetratitanate (550 °C, 2h); (△) adsorption, (+) desorption. Volume of N_2 quoted at STP.

Using the same general procedure, several other layered metal oxides with weaker acidity (such as $H_2Ti_3O_7$ and $H_2La_2Ti_3O_{10}$, *etc.*) can also be pillared by silica to obtain a new class of two-dimensional porous materials with high surface area, which allows for the engineering of microporous materials with diverse compositions and physical properties. In addition, pillaring of these layered materials may lead to new preparative methods for mixed oxide catalysts, in addition to the usual impregnation of the oxide support. Such pillaring may lead to new materials with the catalytic properties of bulk mixed oxides but also with a high surface area.

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