A new pillared structure with double-layers of alumina

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Addition of a suspension of exfoliated titanate nanosheets into an Al_{13} pillaring solution produced a novel pillared structure associated with double layers of Al_{13} cations, which can be converted to a mesoporous alumina-pillared titanate with a 2.4 nm spacing by subsequent heat-treatment.

Pronounced interest has been focused on preparation of layered metal oxides pillared with inorganic compounds. The pillaring process is effective for the formation of porous materials such as molecular sieves, catalyst supports, *etc.*[1] In general, most layered oxides are not easily pillared with bulky inorganic cations owing to their inaccessibility to their interlayer space. It is required to develop new intercalation techniques to form large pillars in layered oxides. One of these technique is the pre-pillaring method, in which the interlayer spacing of the oxides is expanded with long-alkylamine chains[2] followed by intercalation of large inorganic polyoxocations such as $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ ('Al_{13}').

For swollen smectite clays, many routes have been examined to prepare new materials which are thermally more stable and more porous than those pillared by conventional techniques. For example, a pillared montmorillonite with a basal spacing of 2.6 nm was prepared by refluxing or hydrothermally treating a mixed solution of Al_{13} polyoxocations and a salt of a rare earth element (*e.g.* Ce or La nitrate) at 130–200 °C.[3,4] This spacing is much larger than those normally reported for pillared clays,[1] and is believed to result from the formation of large polymeric Ce/La-bearing Al_{13} polyoxocations upon hydrothermal treatment of the solution.[3]

Recently, delamination of various layered host materials has been studied extensively,[5] and restacking of the exfoliated single layers in the presence of the bulky cations gives an alternative route to pillared materials.[6] Sasaki *et al.*[7,8] reported that a layered protonic titanate with lepidocrocite-type structure was exfoliated into its single layers in a tetrabutylammonium hydroxide solution. Here, applying this exfoliation route, we found a novel pillared structure with a double-layer arrangement of Al_{13} polyoxocations. By heat-treatment, this phase was converted into a mesoporous alumina-pillared titanate characterized by a larger interlayer spacing and higher specific surface area in comparison with comparable materials produced *via* a pre-pillaring method.

The layered protonic titanate ($H_{0.7}Ti_{1.83}\square_{0.17}O_4\cdot H_2O$, 1 g) was exfoliated into single sheets upon treatment with 200 cm^3 of a tetrabutylammonium hydroxide (TBAOH) solution (0.016 mol dm^{-3}) for 7 days at room temperature. The ratio of TBA cations to protons in the titanate was adjusted to unity, which is a favorable condition for delamination.[8] The Al_{13} solution was prepared by moderately hydrolyzing an aluminium nitrate solution (0.2 mol dm^{-3}) with tetramethylammonium hydroxide (TMAOH) at room temperature. The OH/Al molar ratio was adjusted to 2.5, where Al_{13} polyoxocations are predominant. The colloidal suspension of the titanate was poured into the Al_{13} solution and aged overnight under stirring at 80 °C. The ratio of Al (mmol)/titanate (g) was 16. The product was collected by centrifugation, washed with distilled water, and dried in air.

Fig. 1(a) shows a powder X-ray diffraction pattern of the protonated titanate with a basal distance of 0.94 nm.[9] The colloidal suspension did not display basal reflections, indicating that the titanate single-sheets were dispersed in the aqueous medium.[8] Addition of the titanate suspension to the Al_{13} solution gave a product with a basal diffraction series of 2.6 nm [Fig. 1(b)]. This new phase with larger spacing has not been reported previously for Al_{13}-pillared materials prepared under such mild conditions. Two possibilities may explain this high expansion: (i) the co-presence of TBA and Al_{13} cations in the interlayer space or (ii) the incorporation of a large amount of aluminium polyoxocations. Thermogravimetry showed only a small broad exothermic peak around 370 °C following a weight loss of 4%, suggesting only a small amount of residual organic cations in the pillared material. After this weight loss, the material had a gallery height of 2.5 nm, and thus indicates that possibility (i) is not valid. Therefore, it can be concluded that the large expansion is mainly due to the presence of a large amount of aluminium polyoxocations in the interlayer space.

The new phase shows two noticeable features in terms of structural and compositional data as compared with the Al_{13}-monolayer pillared titanate: (i) a large interlayer distance of 2.6 *vs.* 1.6 nm (corresponding to intercalation of a monolayer of

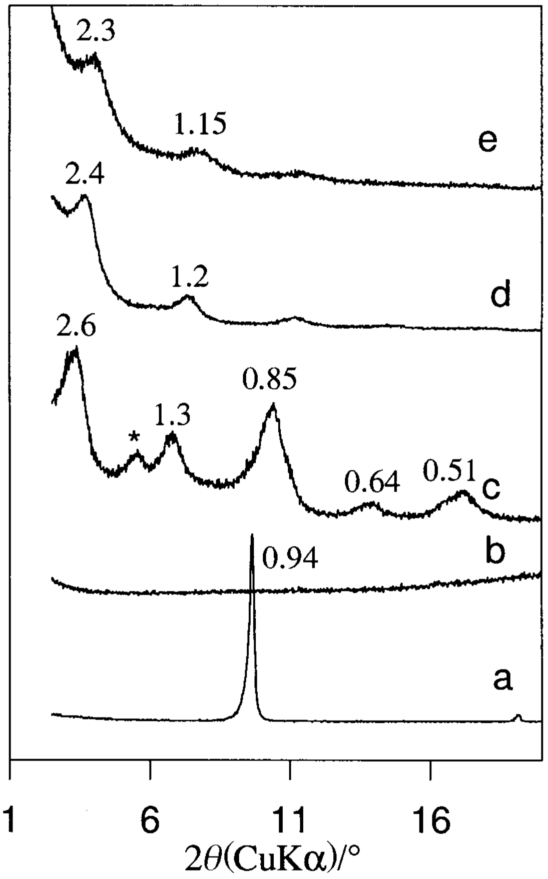

Fig. 1 PXRD patterns of (a) protonated titanate, (b) colloidal suspension of exfoliated titanate and (c) the resulting product prepared after exfoliation and reaction with Al_{13} solution. (d) and (e) correspond to the product (c) heat-treated at 500 and 600 °C, respectively. (*) phase at 1.6 nm (see text).

Al_{13} cations).[10,11] By taking into account the basal spacing of the protonated titanate which accommodates a monolayer of H_2O and H_3O^+, the net interlayer expansion may be estimated as 1.94 nm [= 2.6 − (0.94 − 0.28)]. This is approximately double that of 0.94 nm [= 1.6 − (0.94 − 0.28)] for the monolayered phase.[11] (ii) A double amount of Al_{13} cations. On the basis of chemical analysis, the new product has a composition of $(Al_{13})_{0.22}Ti_{1.83}\square_{0.17}O_4\cdot 2.88\ H_2O$ whereas the amount of Al_{13} cations in the 1.6 nm phase has been reported to be close to 0.11 mol per chemical formula.[11]

These two features strongly suggest that the titanate obtained in this study accommodates Al_{13} cations in a double-layer arrangement. Nazar *et al.*[12] identified a new aluminium polyoxycation cluster formed by the dimerization of two Al_{12} polyoxocations (tentatively formulated as $Al_{24}O_{72}$) which was facilitated by refluxing an Al_{13} solution at high temperatures. This new polyoxycation is about 1.4 nm in size and considerably larger than Al_{13} cations (*ca.* 1 nm).[13] The expected spacing for the intercalation of such a dimeric polyoxocation, however, does not approximate to the large interlayer expansion observed in this study. Furthermore, the formation of the 2.6 nm phase under mild conditions at room temperature should be noted, which excludes formation of the $Al_{24}O_{72}$ polyoxocation.

The Al_{13} polyoxocations are generally believed to hold a theoretical charge of 7+ while the above empirical formula suggests a 3.2+ charge for Al_{13}. A similar situation has also been reported for Al_{13}-intercalated montmorillonite clay.[14] Thus the actual aluminium polyoxocation will probably be modified from $(Al_{13})^{7+}$. Neighboring Al_{13} polyoxocations in a bilayer are expected to mutually condense *via* apical water molecules. Such condensation should be effective in relaxing the electrostatic repulsion between the polyoxocations and lead to charge balance with the host layers interleaving the bilayer. A simple model for the condensation would give the following composition for the modified Al_{13} as $[AlO_4Al_{12}(OH)_{24}O_2(H_2O)_8]^{3+}$.

The intercalation of Al_{13} would probably be irreversible, since the interlayer gallery was little changed before and after treatment of the Al_{13}-product in a solution of sodium chloride (1 mol cm^{-3}) overnight at 80 °C. The pillared structure of the present material was preserved up to 600 °C, while the basal spacing shrunk from 2.6 to 2.4 nm [Fig. 1(c) and 1(d)]. The shrinkage could be attributed to dehydroxylation of the aluminium species upon heating. The pillared material collapsed at 600 °C and TiO_2 and α-Al_2O_3 started to crystallize. The trace '1.6 nm', phase also collapsed.

The sample calcined at 500 °C had a type IV nitrogen adsorption isotherm (in the IUPAC classification) with a large hysteresis loop of type H4.[15] The specific surface area was *ca.* 300 m^2 g^{-1} with a pore volume of 0.25 mL liquid nitrogen per gram of material. The surface area of the pillared titanate was greatly enhanced in comparison with protonic titanate (1–2 m^2 g^{-1}), and also much higher than those of pillared titanates, (100–200 m^2 g^{-1}).[10,11] The average pore diameter is 3.5 nm and the pore size distribution shows a maximum at *ca.* 4.0 nm. Further study is now being conducted to clarify the effect of different experimental parameters on the physico-chemical properties of these materials.

Notes and references

1 K. Ohtsuka, *Chem. Mater.*, 1997, **9**, 2039.
2 A. Clearfield and B. D. Robert, *Inorg. Chem.*, 1988, **27**, 3237.
3 J. Sterte. *Clays Clay Miner.*, 1991, **39**, 167
4 E. Booij, J. T. Kloprogge and A. Rob Van Veen. *Clays Clay Miner.*, 1996, **44**, 774.
5 A. Jacobson, *Mater. Sci. Forum*, 1994, **152**–**153**, 1.
6 L. F. Nazar, S. W. Liblong and X. T. Yin, *J. Am. Chem. Soc.*, 1991, **113**, 5889.
7 T. Sasaki, M. Watanabe, H. Hashizume, H. Yamada and H. Nakazawa, *J. Am. Chem. Soc.*, 1996, **118**, 8329.
8 T. Sasaki and M. Watanabe. *J. Am. Chem. Soc.*, 1998, **120**, 4682.
9 T. Sasaki, M. Watanabe, Y. Michiue, Y. Komatsu, F. Izumi and S. Takenouchi, *Chem. Mater.*, 1995, **7**, 1001.
10 S. Cheng and T.-C. Wang, *Inorg. Chem.*, 1989, **28**, 1283.
11 F. Kooli, T. Sasaki and M. Watanabe, *Microporous Mesoporous Mater.*, in press.
12 L. F. Nazar, G. Fu and D. Bain, *J. Chem. Soc., Chem. Commun.*, 1992, 251.
13 G. Johanson, *Ark. Kemi.*, 1962, **20**, 305.
14 J. Bovey and W. Jones, *J. Mater. Chem*, 1995, **5**, 2027.
15 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. Pierotti, J. Rouquerol and T. Sieminiewska, *Pure Appl. Chem.*, 1985, **57**, 603.

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