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Synthesis and characterization of a new mesoporous alumina-pillared titanate with a double-layer arrangement structure

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Direct reaction of a colloidal suspension of an exfoliated layered titanate with an aluminium polyoxocation solution produced an ordered phase with a large basal spacing of 2.6 nm. Taking into account the starting Al/titanate molar ratio this swelling can be ascribed to the intercalation of double layers of Al_{13} polyoxocations between the titanate sheets. Heat-treatment at 600 °C resulted in an alumina-pillared titanate with specific surface areas ranging from 270 to 300 $m^2\ g^{-1}$ and a pore volume of 0.25 $mL\ g^{-1}$ (liquid nitrogen). The material was mainly mesoporous, the predominant pores having a diameter close to 4.0 nm. The acidity of the pillared titanate was *ca.* 0.60 mmol of protons g^{-1}.

The intercalation of polyhydroxy-cations into layered solids originally focused on swelling clays as host matrices. Intercalation led to thermally stable porous materials after heat-treatment. Among the pillaring agents, the aluminium oligomeric species $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ (known as Al_{13}) has been widely studied.[1] It has been reported that layered metal oxides, such as titanates, may also be pillared with alumina,[2–5] silica[6,7] and chromium oxide[8] *via* a pre-pillaring method. This method generally involves the swelling of the interlayer region by substituted amine cations with long alkyl chains, followed by the exchange of the organic cations with inorganic polyoxocations. Anderson and Klinowski[9] reported that the sodium trititanate could be pillared by direct exchange with Al_{13} cations. However, the ion exchange was incomplete and the starting trititanate was found to remain after the reaction.

Delamination techniques have been developed for various layered materials,[10] and restacking of the exfoliated single layers in the presence of bulky cations produces an alternative route to pillared materials.[11] In addition, novel microstructures, such as heterostructures[12,13] and porous aggregates,[14–16] were constructed by reassembling the exfoliated sheets under controlled conditions. Recently, Sasaki *et al.*[17] have reported that a layered protonic titanate with a lepidocrocite-type structure can be exfoliated into single sheets in a tetrabutylammonium hydroxide (TBAOH) solution. In a previous communication[18] we reported a new pillared structure with a double-layer arrangement of Al_{13} cations between titanate sheets. The new material was obtained by pouring an exfoliated titanate suspension into a solution of Al_{13} cations. Here we describe detailed preparation procedures, optimum experimental conditions and parameters which lead to the formation of pillared titanate with a double-layer arrangement of Al_{13} cations. The resulting materials are characterized by X-ray diffraction, chemical analysis and thermogravimetry, and the textural and acidic properties are also reported.

Experimental

Preparation

The layered protonic titanate $H_{0.7}Ti_{1.83}\square_{0.17}O_4{\cdot}H_2O$ ($\square$ = vacancy; H–Ti) was prepared following the procedure described by Sasaki *et al.*[19] and its exfoliated suspension was prepared by reacting H–Ti (1 g) with 200 cm^3 of TBAOH solution (0.016 mol dm^{-3}) for 7 d at room temperature. The molar ratio of TBA cations to exchangeable protons in the titanate (referred to as TBA/H^+) was adjusted to unity, as this is the most favorable condition for complete delamination.[20]

The pillaring solution (containing mainly Al_{13} cations) was prepared from a solution of aluminium nitrate (0.2 mol dm^{-3}) by hydrolysis at room temperature with tetramethylammonium hydroxide (TMAOH, 0.2 mol dm^{-3}) and ageing overnight at room temperature. The OH/Al molar ratio was adjusted to 2.5, as at this value the Al_{13} polyoxocations are predominant.[5] TMAOH base was used instead of NaOH in order to avoid competition for intercalation between Na^+ and the Al polyoxocations.[5]

The suspension of the exfoliated titanate was poured into the pillaring solution (previously aged at 80 °C for 1 h) and the mixture maintained overnight under stirring at 80 °C. The ratio (*R*) of Al (mmol)/titanate (g) was equal to 16. The product was collected by centrifugation, washed with distilled water, and then dried in air at room temperature. The resulting material will be referred to as S-1680. The same procedure was repeated at room temperature and the sample obtained is designated S-16rt.

Additionally, other samples (S-*R*80) were prepared at 80 °C using different *R*-values. The volume of pillaring solution was kept constant, while the volume of the suspension was varied to reach the desired *R*-value.

To study the effect of the pH of the titanate suspension, different volumes of HCl (0.05 mol dm^{-3}) were added prior to reaction with the Al_{13} solution at 80 °C.

The samples were heat-treated at different temperatures between 300 and 850 °C in air for 4 h. The term "pillared" titanates is used for samples after calcination at 500 °C.

Characterization

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku diffractometer (Rint 2000) with graphite-monochro-

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matized Cu-Kα radiation ($\lambda = 0.15405$ nm). Elemental analysis of Al and Ti was performed by colorimetry and EDTA titration, respectively, after dissolving the sample with a mixed acid solution of H_2SO_4 and HF. The water content was estimated from the weight loss at 900 °C. Thermogravimetric (TG) data and differential thermal analysis (DTA) curves were obtained at a heating rate of 10 °C min^{-1} using a Rigaku TAS 200 thermal analyzer. Specific surface areas (BET), pore volumes and pore size distributions (BJH method) were obtained from the analysis of the nitrogen adsorption–desorption isotherms measured with a Belsorp 28SA instrument. Samples were degassed under vacuum for 8 h at 200 °C prior to the adsorption measurements.

The acidity (surface proton concentration) was determined using the cyclohexylamine adsorption–desorption method.[21] TG analysis was carried out out under a nitrogen flow (25 cm^3 min^{-1}) at a heating rate of 10 °C min^{-1}, and the weight loss measured between 240 and 420 °C was used to estimate the acidity in terms of mmol of cyclohexylamine.

Results

X-Ray diffraction data

Fig. 1 shows the PXRD data for selected samples under pillaring process. The protonic titanate has a basal distance of 0.94 nm (Fig. 1a), while the XRD pattern of the colloidal suspension itself (Fig. 1b) does not show basal reflections, indicating that the layer structure was completely exfoliated.[17,20] The observed broad feature has been attributed to the scattering from dispersed single sheets of the titanate and water acting as a solvent.[20] After the addition of the titanate suspension to the Al_{13} solution at 80 °C, the product dried at room temperature (S-1680) showed a new phase with a basal spacing of 2.6 nm. Additionally, the presence of several diffraction harmonics suggested that the titanate sheets are stacked in an ordered manner (Fig. 1c). Considering the thickness of a dehydrated titanate (0.66 nm),[19] the net interlayer expansion of 1.94 nm is much larger than that expected for the intercalation of a monolayer of Al_{13} ions between titanate sheets.[1,2,5] A similar expansion (Fig. 1d) was observed for the material prepared at room temperature (S-16rt). In addition to the 2.6 nm phase, both products contained traces of a 1.6 nm phase, consisting of a monolayer configuration of Al_{13} ions. Reflections for the S-16rt sample were qualitatively higher in intensity than those for S-1680.

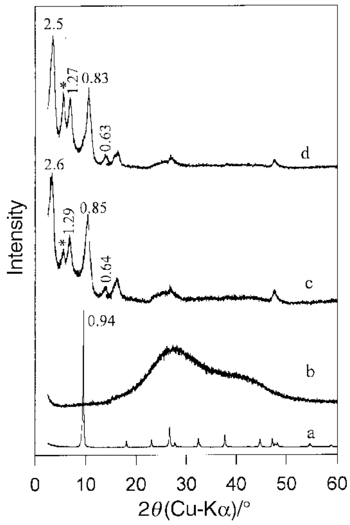

Fig. 1 XRD patterns of (a) the starting protonic titanate, (b) a colloidal suspension of the exfoliated titanate, (c) S-1680 and (d) S-16rt products, obtained at 80 °C and room temperature, respectively. *1.6 nm phase (see text).

Fig. 2 shows that, at $R = 8$, the 2.6 nm phase was not obtained, and only the 1.6 nm phase (S-880) was formed. However, higher doses of Al_{13} ions produced the 2.6 nm phase (S-1680 and S-3280). Larger swellings were not observed when the R-value was further increased above 32 (S-4080).

The 2.6 nm phase was formed in a narrow pH range of the titanate suspension. A slight decrease in pH value, *e.g.* from 12 to 11.64, resulted in an increase in the relative amount of the 1.6 nm phase. The intensity of the 2.6 nm phase decreased steadily with decreasing pH, down to 10.16 where the 1.6 nm phase predominated (Fig. 3). The titanate suspension still remained colloidal at a pH value of 8. Below this value flocculation of the titanate sheets occurred.

Aluminium content

The chemical formulae of the products are given in Table 1. Higher uptake of Al_{13} ions was achieved by exchange at a higher temperature for an R-value fixed at 16. This enhancement is attributed to a higher content of Al_{13} species in the

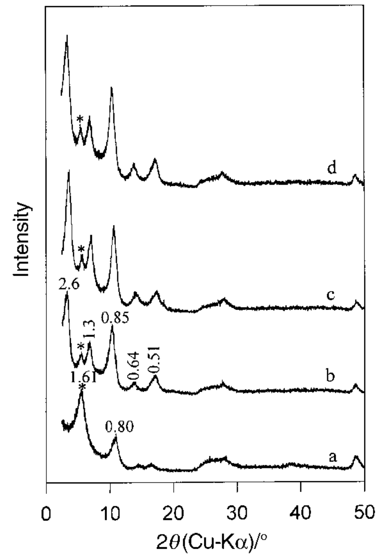

Fig. 2 PXRD data of products prepared with different molar ratios (R). (a) 8, (b) 16, (c) 32 and (d) 40 of Al (mmol)/titanate (g).

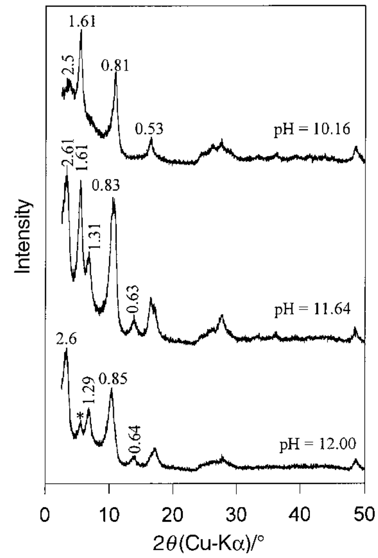

Fig. 3 PXRD patterns of the Al_{13} intercalates prepared from exfoliated titanate suspensions with different pH values. *1.6 nm phase.

Table 1 Chemical formulae, textural properties and acidity of pillared titanates calcined at 500 °C

Precursor	R^a	Formula	S_{BET}/m^2 g^{-1}	$S_{micropore}$/m^2 g^{-1}	Pore volume/mL g^{-1} [N_2(l)]	Acidity/mmol H$^+$ g^{-1}
H–Ti	0	$H_{0.7}Ti_{1.83}\square_{0.17}O_4{\cdot}H_2O$	1–2	^{b}	^{b}	^{b}
S-16rt	16	$(Al_{13})_{0.15}Ti_{1.83}\square_{0.17}O_4{\cdot}2.9H_2O$	194	56	0.24	0.46
S-1680	16	$(Al_{13})_{0.21}Ti_{1.83}\square_{0.17}O_4{\cdot}2.9H_2O$	294	90	0.25	0.58
S-880	8	$(Al_{13})_{0.11}Ti_{1.83}\square_{0.17}O_4{\cdot}2.0H_2O$	154	^{b}	0.27	0.35
S-3280	32	$(Al_{13})_{0.22}Ti_{1.83}\square_{0.17}O_4{\cdot}3.0H_2O$	272	90	0.23	0.60
S-4080	40	$(Al_{13})_{0.22}Ti_{1.83}\square_{0.17}O_4{\cdot}3.2H_2O$	275	95	0.23	0.57

^{a}R indicates the Al (mmol)/titanate (g) ratios in the starting solution. ^{b}Negligible.

solution. Similar observations have been reported for pillared clays[22] and titanates.[3–5] The aluminium content also increased with increasing *R*-values up to 16 and remained constant for higher values. The saturation value is likely to be correlated to the cation exchange capacity.

Thermal stability

The TG curve of S-1680 shows a first weight loss of 13% up to 100 °C, while an endothermal effect centered at 90 °C is observed (Fig. 4); it is assigned to loss of interlayer water and corresponds to 2.9 water molecules per formula unit. A further weight loss up to 400 °C can be attributed to the loss of structural water molecules associated with Al_{13} cations[23] and remaining organic cations. Both weight losses are associated with broad endothermal and exothermal effects at 260 and 325 °C, respectively. The complete dehydroxylation of the oligomers[24] and pillared material occurred above 500 °C where a continuous weight loss is observed.

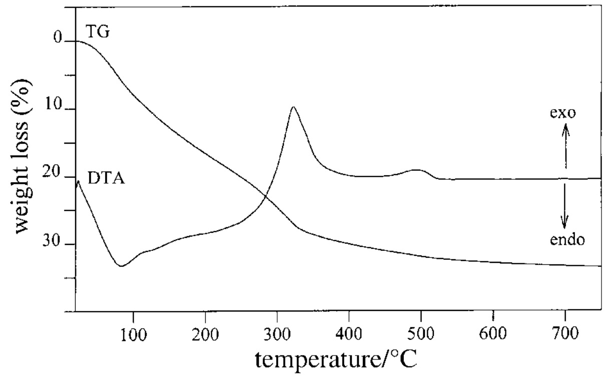

Fig. 4 TG and DTA curves of the S-1680 material.

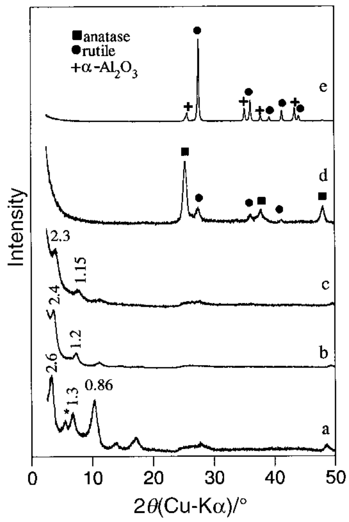

Fig. 5 PXRD patterns of S-1680 heat-treated at different temperatures. (a) As prepared, (b) 500, (c) 600, (d) 750 and (e) 850 °C.

The layered structure of the 2.6 nm phase was stable up to 600 °C (Fig. 5), while existing traces of the 1.6 nm phase collapsed at 500 °C. The shrinkage from 2.6 nm to 2.3 nm (Table 2) was due to dehydroxylation of the aluminium species[25] and to the interaction between the pillars and the titanate sheets.[26] At temperatures above 650 °C, however, the pillared structure was destroyed and a mixture of rutile and anatase phases formed. The transformation of anatase to rutile and separation of the alumina phase was detected at temperatures above 850 °C.

Surface area and porosity

Typical nitrogen adsorption–desorption isotherms for pillared S-1680 calcined at 500 °C are displayed in Fig. 6 and compared with the isotherm of the starting (non porous) protonic titanate. The adsorption isotherm of the pillared titanate is typical of mesoporous solids with a certain contribution from micropores in the lower relative pressure range. A large hysteresis loop of type H3 is observed and is attributable to the presence of slit-shaped pores.[27] The pillared materials prepared under different conditions had similar adsorption isotherms and hysteresis loops.

The textural parameters of pillared titanates calcined at 500 °C are summarized in Table 1. The specific surface areas are much larger than those for the parent titanate before pillaring, and increase with the aluminium content. The micropore surface area (estimated by the *t*-plot method) increases with the amount of aluminium intercalated (Table 1). The microporosity was induced by the pillaring process, and the contribution of the micropore component to specific surface area is between 30 and 35%. These values are lower than those reported for typical microporous pillared materials.[1] The total pore volumes of the different pillared titanates are comparable and unaffected by the aluminium content (Table 1).

As shown in Table 2, the specific and micropore surface areas of S-1680 remain rather constant up to 600 °C and are reduced upon calcination at higher temperatures. The reduction in surface area is ascribed to destruction of the pillars and layered titanates. The total pore volume decreases as a mixture of alumina and titania phases crystallizes above 750 °C.

A typical pore size distribution curve of the pillared titanate S-1680 calcined at 500 °C shows a maximum at 4.0 nm (in diameter) (Fig. 7). The mesopores are derived mainly from the platelet stacking of layered titanates.[26] This mesoporosity is maintained up to 600 °C but lost above 750 °C, and pores 40.0 nm in diameter are formed as a result of destruction of the titanate sheets (Fig. 7). A similar shape of pore size curves has also been observed for pillared materials prepared under different conditions.

Acidity

The acidity values for different pillared titanates calcined at 500 °C are given in Table 1. The pillaring process enhances the acidity in comparison to that of the parent titanate. The surface

Table 2 Basal spacings, specific surface areas and pore volumes of S-1680 titanate calcined at different temperatures (°C)

Precursor	Basal spacing/nm	S_{BET}/m^2 g^{-1}	$S_{micropore}$/m^2 g^{-1}	Pore volume/mL g^{-1} [N_2(l)]
S-1680(25)	2.6	137	45	0.14
S-1680(300)	2.5	300	96	0.25
S-1680(500)	2.4	294	90	0.25
S-1680(600)	2.3	292	80	0.26
S-1680(750)	[a]	107	[b]	0.20
S-1680(850)	[a]	21	[b]	0.08

[a] Layered structure was destroyed. [b] Negligible.

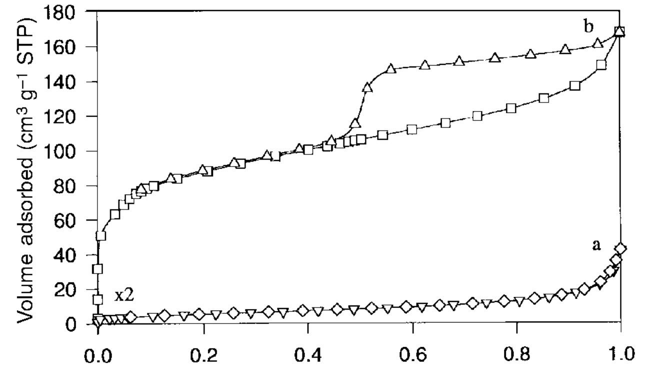

Fig. 6 Nitrogen adsorption–desorption isotherms of (a) starting protonic titanate and (b) S-1680 heat-treated at 500 °C.

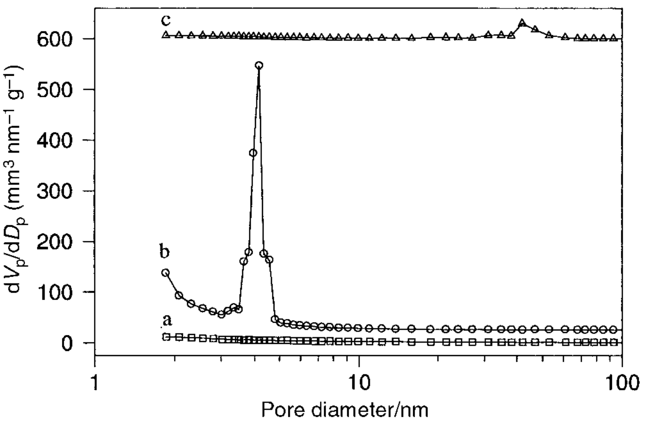

Fig. 7 Pore size distribution of (a) the protonic titanate and pillared S-1680 heat-treated at (b) 500 and (c) 850 °C, respectively.

concentration of acid sites in the pillared materials depends upon the synthesis conditions. The acidity of the pillared titanate prepared at 80 °C (S-1680) is higher than that of S-16rt prepared at room temperature. The pillared titanate (S-880) has the lowest acidity, as a result of having the lowest aluminium content. The acidity values are coincident, within experimental error, for the pillared S-1680, S-3280 and S-4080 titanates, due to the similarity in the amounts of intercalated Al (see Table 1).

Discussion

Structural and compositional data of the new 2.6 nm phase suggest two noticeable features as compared to those of the Al_{13}-pillared titanates prepared by way of the pre-swelling followed by ion-exchange procedure. (i) The net interlayer expansion of 1.95 nm is *ca.* twice that of the monolayer intercalated phase (0.94 nm). (ii) This new phase contains approximately twice the amount of Al_{13} ions existing in the monolayer phase (S-880 in Table 1).

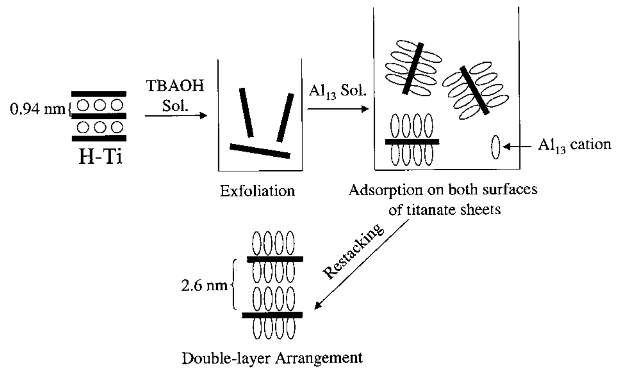

Fig. 8 Schematic explanation for the pillaring process with a double-layer of Al_{13} cations.

These two features suggest with that our pillared titanate hosts Al_{13} ions in double-layer arrangement. Aznar *et al.*[28] have reported the formation of a new polyoxocation cluster of polymerized Al_{12} units by refluxing Al_{13} solutions at high temperatures. The radius of this new cluster (Al_{24}), at *ca.* 0.7 nm, is larger than that of the Al_{13} species (0.5 nm). Monolayer arrangement of such a dimer would give a basal spacing of 2.1 nm, which is smaller than that observed in this study. Moreover, the fact that the 2.6 nm phase was obtained even at room temperature could exclude the possibility of intercalation of the dimeric (Al_{24}) Keggin ions.

It is essential to use exfoliated titanate sheets for the formation of the 2.6 nm phase. The formation of the double-layered phase may involve adsorption of polyoxocations on both surfaces of the exfoliated titanate sheets, followed by restacking, as schematically shown in Fig. 8. The proposed mechanism is similar to that reported for the pillaring of α-zirconium phosphate with chromium polyoxocations[29] and for the preparation of layered nanocomposites of organic polymers and montmorillonite clay or molybdenum disulfide.[30,31]

The chemical composition obtained for the 2.6 nm phase indicates that the charge on the intercalated Al_{13} cations is 3.2+, although formally it should be 7+. Similar deviation of the charge has been also reported in the case of Al_{13}-intercalated montmorillonite clay.[32,33] This deviation suggests that the actual aluminium polyoxocation would be modified from $(Al_{13})^{7+}$. One of the proposed models,[17] resulting from the condensation of neighboring Al_{13} polyoxocations, would give the composition $[AlO_4Al_{12}(OH)_{24}O_2(H_2O)_8]^{3+}$ for modified Al_{13} ions.

The pillaring reaction provides a new route to microporous materials. Alumina pillared clays are known to be predominantly microporous,[34] but the alumina pillaring species can be modified (*e.g.*, by doping with lanthanum[35] or iron[36]) and the resulting pillared clays contain a significant amount of mesoporosity between the clay particles.[36] The new pillared titanates prepared here, with a large interlayer spacing of 2.4 nm, have a specific surface area of 270 to 300 m^2 g^{-1}. These values are higher than those of pillared titanates (100 to 200 $m^2 g^{-1}$) prepared *via* the conventional process of pre-swelling and ion exchange.[3–5] The low micropore surface areas are related to the amount of Al in the pillared materials. The hysteresis loop shows a distinguished capillary condensation which is characteristic of mesopores. The pore volume (*ca.* 0.25 $mL g^{-1}$) was independent of aluminium contents and calcination temperatures up to 600 °C. In addition, the similarity between the pore size distribution curves of different pillared titanates (with a maximum at a diameter of 4.0 nm) suggests that the mesoporosity is mainly created between the titanate platelets during the synthesis process.

Concluding remarks

Pillaring of the titanate with double layers of Al_{13} cations was achieved by exfoliation and subsequent restacking in the presence of Al_{13} cations. The new pillared structure was formed in a narrow range of preparative conditions with respect to pH and dose of Al_{13} polyoxocation solution. Calcination at 500 °C produced the mesoporous alumina pillared titanate with a surface area of 300 $m^2 g^{-1}$. The increase in the surface areas of the pillared materials is related to the creation of some micropores but mainly of mesopores (4 nm in diameter) during the restacking of the titanate sheets.

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