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Characterization and acidic properties of silica pillared titanates

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Reaction of alkylammonium titanates with tetraethylorthosilicate (TEOS) resulted in the intercalation and polymerization of TEOS between the titanate sheets. After heating to 500 °C, the basal spacing of pillared silica titanates increased with increasing length of the alkylamine chains and the amount of silicon intercalated. Although the layers of pillared titanates were expanded by the silica species, and the specific surface area increased, only negligible micropores were formed, suggesting that the interlayer region was "stuffed" with the pillaring species. The adsorption of pyridine indicated the formation of strong Brönsted acid sites up to 300 °C. In addition some basic Lewis sites were detected on silica pillared titanates.

Pillared interlayer clays (PILCs) and layered materials have received widespread interest as a new type of microporous solid.[1,2] However, the large thermal stability, surface area and permanent microporosity of these pillared solids deteriorate at 500 °C in practical applications, especially during the regeneration of deactivated catalysts.[1] Many attempts have been made to overcome this problem, *e.g.* introducing mixed metal oxide pillars.[3–5] Silica is one of the more interesting oxides for the preparation of thermally stable, catalytically active pillared clays.[6] The negative surface charge of the silica sol can be modified with metal polyhydroxy cations and intercalated into montmorillonite.[7–9] The resulting pillared clays exhibit a high thermal stability up to 800 °C with large basal spacing (up to 6 nm) and surface area ($\sim 700\ m^2\ g^{-1}$).

By analogy with clays, titanates can be pillared to produce thermally stable and porous materials after subsequent calcination. Such titanates have been pillared by indirect stepwise intercalation which involves swelling of titanate with hexylamine followed by an exchange with aluminium polyoxocations.[10,11] The resulting microporous materials had a surface area of 100 to 200 $m^2\ g^{-1}$. The chromia pillared tetratitanate (with a surface area of 94 $m^2\ g^{-1}$) was prepared by the reaction of layered tetramethylammonium-intercalated tetratitanate with an aqueous chromium(III) acetate.[12] As for the lepidocrocite-type layered titanate, we have recently demonstrated that a new pillared titanate with a double-layer arrangement of alumina was obtained by flocculating a colloidal suspension of an exfoliated titanate with Al_{13} Keggin ions. In this case a higher surface area ($\sim 300\ m^2\ g^{-1}$) associated with mesopores was acheived.[13] Landis *et al.*[14] reported the pillaring of the disodium trititanate by tetraethylorthosilicate (TEOS). The calcined samples exhibited high surface areas from 200 to 470 $m^2\ g^{-1}$. Sylvester *et al.*[15] intercalated (3-aminopropyl)trimethoxysilane into potassium tetratitanate from a colloidal suspension of propylamine titanate. However, the resulting pillared titanate had a low surface area of only 42 $m^2\ g^{-1}$. Yamanaka *et al.*[16] prepared a pillared titanate $Rb_xMn_xTi_{2-x}O_4$ ($x = 0.75$) with silica. The resulting microporous materials had high surface areas of 500–800 $m^2\ g^{-1}$ and thermal stability up to 600 °C. However, the acidic properties of silica pillared titanates were not reported in these studies. We are interested in the preparation of silica pillared titanates starting from a layered titanate different to that used by Yamanaka *et al.*[16] ($H_{0.7}Ti_{1.83}\square_{0.17}O_4\cdot H_2O$, $\square$ = vacancy) using TEOS as the pillaring agent. This paper reports the characterization and acidic properties of these materials using a variety of molecular probes.

Experimental

Synthesis

A titanate of $Cs_{0.7}Ti_{1.825}\square_{0.175}O_4$ ($\square$ = vacancy) was prepared *via* the solid-state reaction of Cs_2CO_3 and TiO_2 at 800 °C for 20 h, repeated twice. The protonated form of Cs-titanate (abbreviated as H-Ti) $H_{0.7}Ti_{1.83}\square_{0.17}O_4\cdot H_2O$ was prepared by leaching Cs-titanate in aqueous HCl solution (1 mol dm^{-3}) at room temperature, the leaching was repeated (four times in total) by replacing the solution with a fresh one every 24 h.[17] Different n-alkylamines such as n-butylamine, n-hexylamine and n-nonylamine were used to pre-expand the protonic titanate prior to the pillaring process. Then 2 g of H-Ti were mixed with 200 cm^3 of n-alkylamine solution (0.1 mol dm^{-3}) and shaken for 5 days. The solid was separated by filtration, washed with hexane and air-dried at room temperature.[18]

To intercalate tetraethylorthosilicate (TEOS), 0.5 g of the n-alkylamine intercalated titanate was mixed with 44 cm^3 of TEOS (corresponding to 400 mmol of Si per g of titanate) at 80 °C overnight with constant stirring. The intercalated product was separated by centrifugation, washed with a 1 : 1 mixture of ethanol and water, then air-dried at room temperature. The samples prepared from n-alkylamines are abbreviated as C*x*-TiSi80, where *x* is the number of carbon atoms in the alkyl chain, and that prepared from H-Ti is abbreviated as H-TiSi80 (in both cases 80 refers to the temperature used during the intercalation). For comparison, TEOS was also intercalated at room temperature using

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hexylammonium titanate (C6-Ti) as the host material (C6-TiSiRT).

The different samples were calcined in the temperature range from 300 to 600 °C, at a heating rate of 10 °C min^{-1} for 4 h under an air atmosphere. The term "pillared" was used for samples after calcination at 500 °C.

Characterization

Powder X-ray diffraction patterns (PXRD) were collected on a Rigaku Rint-2000 diffractometer with copper radiation ($\lambda = 0.15405$ nm). An ICP spectrophotometer model SII 1700HVR was used for elemental analysis of Ti and Si. Chemical analyses of C, H, and N were obtained using a CE instruments CHN analyser (model EA 1110). Thermogravimetric analyses were obtained at a rate of 10 °C min^{-1}. ^{29}Si MAS NMR was performed on a Bruker AMX 500 solid NMR spectrophotometer. The adsorption–desorption isotherms of nitrogen were determined on a Belsorp 28SA instrument. Samples were degassed at 200 °C for 8 h prior to the measurements. Specific surface areas (estimated using the BET equation) and total pore volumes were determined using a computerized program developed by Rives.[19]

The acid content of the pillared titanates was estimated by the cyclohexylamine adsorption–desorption method.[20] The thermogravimetric analyses were performed on a Mac-Science TGA-DTA 2000S instrument under a nitrogen gas flow of 25 cm^3 min^{-1}. The acid content (in mmol of cyclohexylamine per gram of sample) was computed from the weight loss between 240 and 420 °C. It was assumed that each mole of cyclohexylamine interacted with one mole of protons.

Adsorption of pyridine, boric acid trimethyl ester (BATE) and formic acid was carried out as follows. The pillared titanate (50–60 mg) was compacted to a self-supported disc (1 cm diameter) and then calcined in air at 400 °C for 2 h in the same cell in which the spectra were recorded in order to eliminate adsorbed organic impurities. The sample was then outgassed at 400 °C for 2 h at a residual pressure of *ca.* 10^{-4} N m^{-2}. It was equilibrated at room temperature at a pressure of 0.2 kN m^{-2} for adsorption of pyridine or BATE, or 1 kN m^{-2} for the adsorption of formic acid, and then outgassed for 30 min at different temperatures up to 400 °C. The Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer FT-IR 16 PC instrument after each outgassing treatment (averaging 100 spectra at a nominal resolution of 2 cm^{-1}). Using the software provided, the spectrum of the parent solid outgassed at 400 °C was subtracted from the spectra recorded after adsorption.

Results and discussion

Powder X-ray diffraction

The basal spacing of the n-alkylammonium intercalated titanates (Fig. 1) increased with alkyl chain length. The increment was 0.17 to 0.19 nm. In the case of the mixed alkali metal titanate with a lepidocrocite-like structure, the n-alkylammonium ions were packed in interdigitated single layers which were perpendicular to the titanate sheets.[18]

After reaction with TEOS at 80 °C (Fig. 2) the interlayer distance in H-TiSi80 did not increase, indicating that TEOS was not intercalated. However, TEOS was taken up by the n-alkylammonium titanates, the basal spacing increasing with alkyl chain length. These data illustrate the importance of pre-swelling H-Ti with n-alkylamine prior to the intercalation of TEOS.[11,21] The C6-TiSiRT sample had a basal spacing of 2.06 nm, somewhat smaller than that of C6-TiSi80 (2.24 nm).

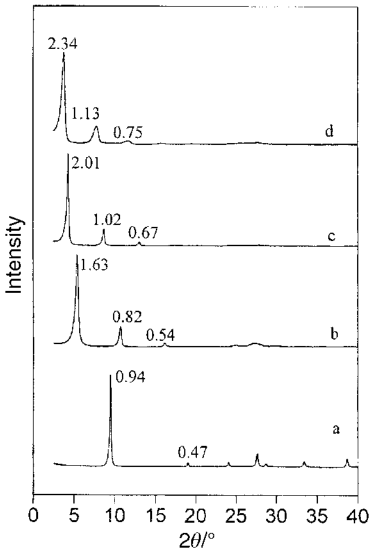

Fig. 1 PXRD patterns of starting protonic titanate (a) and intercalated with different alkylammonium cations: (b) C4, (c) C6 and (d) C9.

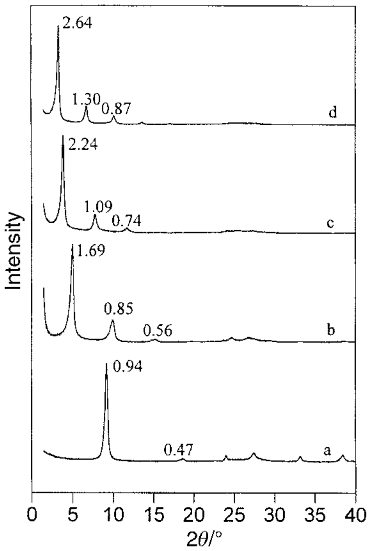

Fig. 2 PXRD data of protonic titanate and alkylammonium titanates reacted with TEOS at 80 °C for 18 h (details as for Fig. 1).

Silicon content

The elemental analysis data for the TEOS intercalated titanates are presented in Table 1. The nitrogen content was assumed to be due to the presence of ammonium cations and indicated that their exchange with TEOS was incomplete. The percentage of nitrogen present in the TEOS intercalated titanates decreases as the amount of TEOS increases, suggesting that the exchange of the ammonium cations is more effective at higher TEOS concentrations. The amount of TEOS incorporated increased with the alkyl chain length used (Table 1) suggesting higher

Table 1 Composition (wt%) of TEOS intercalated titanates

Sample	C4-SiTi80	C6-SiTi80	C9-SiTi80	C6-SiTiRT
SiO_2	16.71	19.07	21.00	18.20
TiO_2	60.38	54.34	50.37	55.87
C	8.03	9.75	13.28	11.25
H	2.80	2.97	3.80	3.63
N	1.95	1.67	1.52	2.15
H_2O^a	7.80	9.65	9.49	8.75

^{a}Weight loss below 200 °C from TGA.

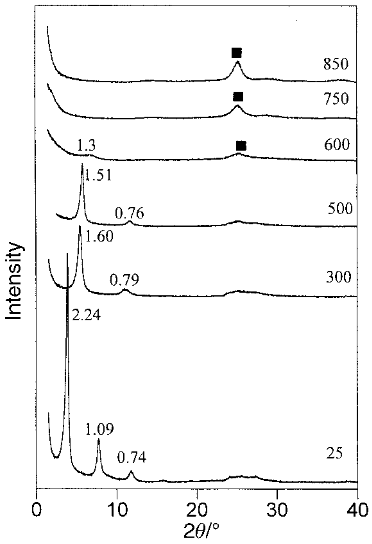

Fig. 3 PXRD patterns of C6-TiSi80 calcined at different temperatures (°C). The symbol ■ denotes peaks corresponding to anatase.

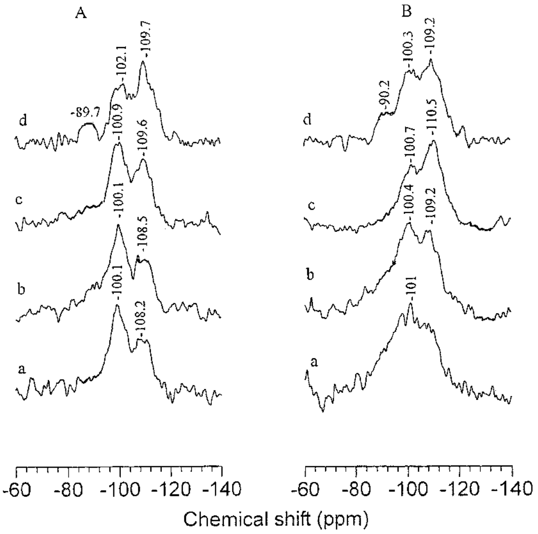

Fig. 4 ^{29}Si MAS NMR spectra for TEOS intercalated titanates (A) before and (B) after calcination at 500 °C in air. (a) C4-TiSi80, (b) C6-TiSi80, (c) C9-TiSi80 and (d) C6-TiSiRT.

accessibility of TEOS into the more open interlayer spaces.[22] A higher reaction temperature also raised the amount of silicon that was intercalated.

Thermal stability

The heat-treatment of C6-TiSi80 at different temperatures (Fig. 3) indicated a significant change at 300 °C, the basal spacing decreased from 2.24 nm to 1.60 nm as a result of decomposition of the organic moiety. This structure was maintained up to 500 °C, accompanied by a slight contraction. Similar basal spacing of 1.6 nm was obtained for C9-SiTi80 and C6-SiTiRT, while a smaller value of 1.2 nm was obtained for the C4-SiTi80 pillared material. The layered structure totally collapsed at 600 °C and an anatase phase began to crystallize. The C, H, N chemical analysis of pillared titanates (about 0.2%) indicated that the organic moieties were present in only trace amounts and completely decomposed after calcination at 500 °C.

The parent titanate (H-Ti) accommodates monolayer oxonium ions in its interlayer space.[17] The layer thickness may be calculated to be 0.66 nm ($=0.94-0.28$) by taking the size of H_3O^+ as 0.28 nm. By taking this into account, the height of the silica pillars is in the range 0.5–0.9 nm. The height of 0.5 nm observed for pillared C4-TiSi80 was larger than expected for the intercalation of a single SiO_2 layer (0.3 nm)[23] and implies formation of silicate species containing two layers of Si atoms (0.6 nm).[24] The expansion of 0.9 nm for C6-TiSi80 and C9-TiSi80 pillared materials could result from the presence of $[Si_8O_{12}]^{8+}$ species which has been suggested for silica pillared tetratitanate.[15] The size of the silicate polymers was dependent upon the pre-swelling distance of the titanate layers and was explained by the *in situ* formation of silicate polymers in the gallery.[14]

^{29}Si MAS NMR

The ^{29}Si MAS NMR spectra for the pillared titanates before and after calcination at 500 °C are presented in Fig. 4. All the TEOS intercalated titanates exhibited mainly two peaks before calcination at around -100 and -109 ppm assigned to Si in Q^3 and Q^4 environments.[25] An additional peak was observed for C4-SiTi80 at -89.7 ppm which was probably due to the incomplete hydrolysis of TEOS at room temperature.[26] In the case of layered niobium oxides intercalated with TEOS, only one peak was observed at around -98 ppm.[26] After calcination, similar spectra were obtained for pillared titanates C6-TiSi80 and C9-SiTi80, with two peaks appearing around -100 and -109 ppm (assigned to Q^3 and Q^4 environments for Si). However, broad peaks were obtained for the C4-TiSi80 pillared material, indicating the formation of different silicon species. The detection of a Q^4 peak in the pillared titanates could indicate that the silica pillar consisted of Q^3 and Q^4 Si, and/or formation of a silica-like structure even before calcination occurred.[27]

Surface area and porosity

The nitrogen isotherms for the pillared titanates and H-TiSi80 are depicted in Fig. 5 and showed mesoporous features only at high relative pressures. No hysteresis loop was observed. The isotherms were not completely reversible, suggesting some chemisorption.[28]

The specific surface areas and total pore volumes are listed in Table 2. The H-TiSi80 material exhibited a very low surface area of 8 $m^2\ g^{-1}$. However, the surface area of the pillared titanates was dependent on the amount of silica adsorbed, ranging from 27–102 $m^2\ g^{-1}$. The low surface area (27 $m^2\ g^{-1}$)

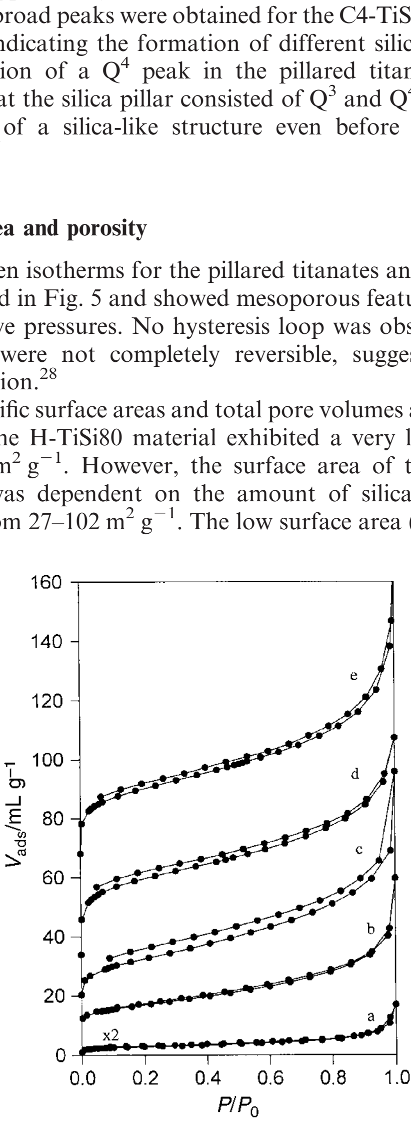

Fig. 5 Nitrogen adsorption–desorption isotherms of protonic titanate and n-alkylammonium titanates reacted with TEOS then calcined at 500 °C. (a) H-TiSi80, (b) C4-TiSi80, (c) C6-TiSi80, (d) C9-TiSi80 and (e) C6-TiSiRT.

Table 2 Surface area, pore volume and acidity of the pillared titanates calcined at 500 °C

Precursor	Surface area/ $m^2\ g^{-1}$	Pore volume/ $mL\ g^{-1}$	Acidity/ mmol $H^+\ g^{-1}$
H-Ti	1–2	[a]	[a]
H-TiSi80	8	0.012	[a]
C4-TiSi80	27	0.045	0.20
C6-TiSi80	62	0.083	0.50
C9-TiSi80	102	0.100	0.76
C6-TiSiRT	88	0.098	0.65

[a] Negligible.

for C4-TiSi80 may be due to a smaller silica content and basal spacing. The highest surface area was observed for C9-TiSi80 which also had the largest silica content and interlayer expansion but the microporous volume observed was very small. This may suggest that the interlayer space is stuffed, or that there are very small pores between the silica pillars which are inaccessible for nitrogen molecules. The relatively high pore volumes were probably due to the mesopores resulting from the defects incurred through pillaring and calcination or to the excess of silica species adsorbed onto the titanate particles.

Acidity characterization

Brönsted acidity. The acid content of different pillared silica titanates is given in Table 2. The incorporation of silica generated acid sites and their population increased with silicon content. The acidity of C6-TiSi80 (0.50 mmol $H^+\ g^{-1}$) was lower compared to C6-TiSiRT (0.65 mmol $H^+\ g^{-1}$), although the silicon content was higher.

Brönsted and Lewis acidity. The FT-IR spectrum of pyridine adsorbed on H-Ti (calcined at 500 °C) has been reported previously[29] and showed absorption bands at 1604, 1575, 1490 and 1445 cm^{-1}, ascribed to the modes 8a, 8b, 19a, and 19b of pyridine bound to Lewis acid sites (coordinatively unsaturated Ti^{4+} ions). No bands were detected for the pyridinium ion. The Lewis acid sites were rather strong and were also detected after outgassing the sample at 300 °C. On the other hand, pyridine physisorbed on silica gave bands at 1596 and 1447 cm^{-1}. These bands were completely removed after outgassing at 100 °C and their positions coincide with those reported elsewhere.[30,31]

The spectrum of C4-TiSi80 (Fig. 6) shows, before outgassing, absorption bands at 1635, 1605, 1587, 1575 (shoulder), 1544, 1488, 1446 and 1437 cm^{-1} (shoulder). The bands at 1635 and 1544 cm^{-1} correspond to modes 19b and 8a of protonated pyridine. These two bands were intensified after outgassing at room temperature, while the broad band of physisorbed pyridine disappeared. The other bands survived, even after outgassing at 300 °C (not shown). These results indicate that the C4-TiSi80 pillared titanate contains both Lewis and Brönsted acid sites. The formation of Brönsted acid sites suggests the presence of some interactions between titanate sheets and pillaring species. We previously reported a similar generation of Brönsted sites upon pillaring of titanate with alumina.[29]

The spectra of C6-TiSi80 (Fig. 7) and C9-SiTi80 were very similar to that described above for pillared C4-TiSi80. It should be noted that the bands (1605 and 1446 cm^{-1}) due to modes 8a and 19b of coordinated pyridine are split, especially for sample C9-TiSi80, probably due to the presence of surface Lewis acid sites with different acid strengths, usually related to Ti^{4+} ions in different coordination sites.

Tanabe *et al.*[32] reported that Lewis acid sites were generated by incorporation of silicon into the TiO_2 matrix, while Brönsted acid sites were produced by incorporating titanium into SiO_2. As a result, mixed oxides with different degrees of acidity could be prepared by varying the composition. For example, Doolin *et al.*[33] examined the acidity of a mixed titania–silica oxide prepared by a coprecipitation or sol–gel method with a silicon content varying from 0 to 100 wt%. An oxide with a Si : Ti molar ratio of 0.11 was the most acidic. However, in our case, pillaring titanate with TEOS led to acidic material with a Si : Ti molar ratio of 0.55.

Surface basicity. Surface basicity was assessed by the adsorption of BATE and formic acid onto the surface. BATE is a very sensitive probe molecule which permits the detection of Lewis basic sites on the solid surface. During the interaction of BATE with the surface its planar structure is deformed leading to the ν(B–O) bands splitting and shifting to lower wavenumber.[34]

The spectra of the pillared titanates after BATE adsorption were very similar; a typical spectrum obtained for C4-SiTi80 is shown in Fig. 8. Bands were recorded at 1485 [$\delta(CH_3)$], 1390, 1363, and 1307 [ν(B–O)], and 1090 and 1060 cm^{-1}. The $\delta(CH_3)$ band at 1485 cm^{-1} was not changed by adsorption of BATE; however, the ν(B–O) band at 1363 cm^{-1} for pure BATE was split, and an additional doublet recorded at 1390 and

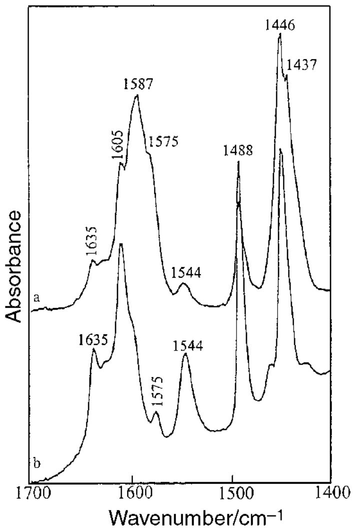

Fig. 6 FT-IR spectra corresponding to the adsorption of pyridine on pillared C4-TiSi80 titanate at (a) room temperature and (b) after outgassing at 100 °C.

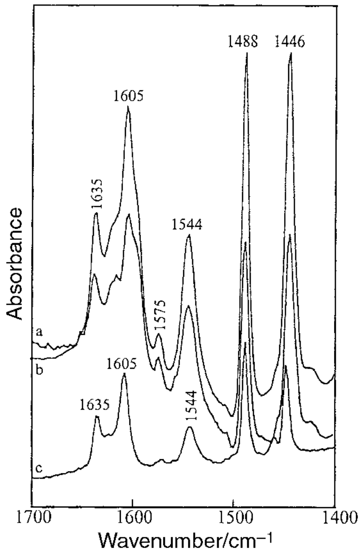

Fig. 7 FT-IR spectra corresponding to the adsorption of pyridine on pillared C6-TiSi80 titanate (a) and after outgassing at different temperatures: (b) 200 °C and (c) 300 °C, respectively.

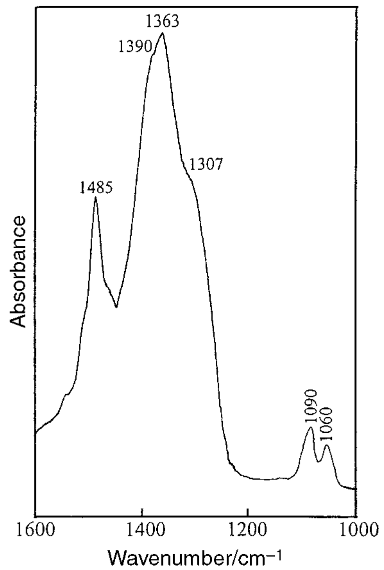

Fig. 8 FT-IR spectrum recorded after adsorption of BATE onto pillared C4-TiSi80 titanate at room temperature.

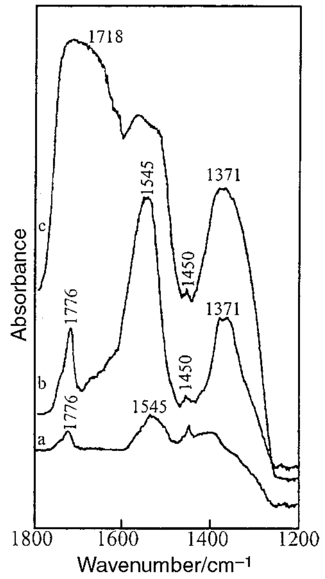

Fig. 9 FT-IR spectra corresponding to adsorption of formic acid on pillared C4-TiSi80 titanate: (a) as prepared; and after outgassing at (b) room temperature and (c) 200 °C.

1307 cm^{-1}. Also, two bands were observed at 1090 and 1060 cm^{-1}, ascribed to ν(C–O). We conclude that a weak interaction of BATE with pillared titanates did not change the position of the bands corresponding to pure BATE. Unfortunately we can not differentiate between ions with different coordination symmetries, or with different electron densities. The results reported were similar to those previously reported for the adsorption of BATE onto TiO_2 and ZrO_2.[34,35]

The adsorption of formic acid (Fig. 9) gave rise to strong IR absorption bands, at 1718, 1545, 1450, and 1371 cm^{-1}, which are attributed to ν(C–H), ν_{as}(COO), $\delta(CH_3)$ and ν_s(COO) modes of surface formate species (dissociative adsorption). The strong band at 1718 cm^{-1} was due to adsorbed undissociated formic acid. The intensity of these bands, particularly those corresponding to molecularly adsorbed formic acid, decreased sharply at higher outgassing temperatures. The other bands were recorded even after outgassing at 300 °C, thus confirming the presence of strong basic sites on the surface.

Formate ions can coordinate in three different ways: (a) as a monodentate ligand, (b) as a bidentate bridging ligand, and (c) as a bidentate chelate ligand. Several authors[36,37] have claimed that the difference between the positions of the bands due to ν_{as}(COO) and ν_s(COO) indicates the mode of coordination. In our case, $\Delta\nu$ was equal to 174 cm^{-1} and it is difficult to discriminate between coordination modes (b) and (c).

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