Preparation and characterization of L-tartaric acid–silica composites recognizing molecular asymmetry

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L-Tartaric acid–silica composites have been prepared by the sol–gel method in which tetraethoxysilane is hydrolysed after reacting with L-tartaric acid. Optical resolution of tris(pentane-2,4-dionato)metal complexes was performed using sol–gel derived composites and composites prepared using a conventional impregnation technique. The composites prepared through the sol–gel process showed much higher optical resolution abilities when the composite was used for packing in chromatography. X-Ray diffraction and NMR results suggested that L-tartaric acid in the sol–gel derived composites is highly dispersed because it bonds to silicon atoms. The silica gel support was observed by scanning electron microscopy to be composed of small particles whose diameters are below 30 nm. The asymmetry recognition ability of the composites was found to arise from the combined effect of the silica support and the highly dispersed optically active compound.

Materials with molecular recognition ability are of great importance in fields such as separation, sensing and catalysis. Organic–inorganic composites exhibit not only the properties of both the constituents but also often have entirely new properties.[1] Many composites comprising silica and an optically active organic compound have been prepared and used in chromatography.[2–14] However, they are usually limited to two classes, one in which an optically active organic compound is covalently coupled to a functional group pendant on the silica surface through C—Si bonds such as aminopropyl-derivatized silica,[2–9] and the other in which the silica surface is coated with an optically active compound such as cellulose.[10–14] In these compounds, silica is used as a support to fix an optically active compound and no further role other than that of a support is expected.

We have studied the preparation of metal oxides through the sol–gel process using organic ligands as modifiers; however, the organic modifier was finally removed by calcination.[15–19] We considered that a composite incorporating an optically active compound in the skeleton structure of silica should have different properties compared to a composite bearing an optically active compound on the silica surface. It might show a certain synergism of the combined effect of the adsorptive ability of silica and the molecular recognition ability of an optically active compound in separation. We have reported the resolution of optically active compounds by using sol–gel derived organic–inorganic composites such as D-lactose–silica.[20] Accordingly, we have carried out further investigations on composites. Here, we report the incorporation of L-tartaric acid as an optically active organic material in silica gel through a sol–gel procedure. The optical resolution of tris(pentane-2,4-dionato)cobalt(III) with L-tartaric acid–silica composites and the structures of the composites including the chemical state of L-tartaric acid in the silica matrix are also reported.

Experimental

Preparation of composites using TEOS and L-tartaric acid

Sol–gel composites. Commercial tetraethoxysilane (TEOS, Kanto Chemical), L-tartaric acid (Wako Pure Chemical) and propan-2-ol (Wako Pure Chemical) were used without purification. In a 500 cm^3 beaker, 0.6 mol of TEOS was mixed with L-tartaric acid (0.1–0.8 mol) in 1.66 mol of propan-2-ol in the presence of acetic acid (0.2 mol). The reaction mixture was kept in an oil bath at 80 °C for 2 h under stirring. During heating, gaseous propan-2-ol and ethanol were liberated from TEOS. 1.2 mol of deionized water ($H_2O/TEOS = 2$) was then added to the reacted viscous solution. After stirring at 80 °C for 2–6 h, the solution turned into a viscous sol, and finally coagulated. After this, the gel was aged at the same temperature for a further 15 h, the aged wet gel dried under a reduced pressure of *ca.* 40 Torr in a rotary evaporator at 80 °C for 2 h, and then ground to a powder. The composite powder [<200 mesh (74 μm)] was used as the chromatographic packing reagent.

Impregnation composites. For comparison, composites were also prepared by a conventional impregnation method, in which silica powder was first prepared from TEOS in a similar way to above but without tartaric acid, and impregnated with an ethanol solution of tartaric acid at 80 °C for 1 h. The solutions used for impregnation contained 0.05, 0.1, 0.2, 0.3 or 0.4 mol of tartaric acid in 200 ml of ethanol. The dried gels were ground and sieved in the same manner as described above. In all the composites prepared, the content of L-tartaric acid was checked by thermogravimetry–differential thermal analysis (TG–DTA). The L-tartaric acid : SiO_2 ratio was found to be almost equal to the ratio used in the preparation.

Packing and elution

In order to monitor the molecular recognition ability, the composites were used as chromatographic packings by a simple technique; all the composites were ground to below 200 mesh and were slurried with *n*-hexane and packed in a glass tube of 6 mm i.d. × 400 mm in length and a small amount of a benzene solution of racemic tris (pentane-2,4-dionato)cobalt(III) [$Co(acac)_3$, Wako Pure Chemical] was placed on a column and eluted with *n*-hexane–benzene (1 : 1, v/v) without any artificial pressure.

Measurements and characterization

Circular dichroism (CD) spectra were recorded on a JASCO J-600 spectropolarimeter. X-Ray diffraction (XRD) patterns were recorded on a MAC Science MPX 18 using nickel-filtered Cu-Kα radiation. TG–DTA was carried out on a MAC Science TG–DTA 2100 instrument with a heating rate of 10 °C min^{-1} under a flow of 100 cm^3 min^{-1} dry air. The IR spectra were measured using a Shimadzu FTIR-8500 IR spectrophotometer.

Solutions were studied by putting a droplet on a KBr window and gels and solids were studied as powders dispersed in a KBr pellet. Solid-state ^{13}C CP MAS and ^{29}Si MAS NMR spectra were recorded on a Brüker AMX500 spectrometer (125.78 and 99.366 MHz, respectively). A spinning speed of 4000 Hz and a delay time between pulses of 10 s were employed. Scanning electron microscopy (SEM) was performed on a Hitachi S-800 instrument. Specific surface areas were measured by the BET method based on the adsorption of N_2 at 77 K using a Belsorp36 instrument (BEL Japan). Pore size distribution and pore volume were evaluated by analysing N_2 desorption isotherms according to the Dollimore–Heal method.[21] The external surface area was determined by the *t*-plot method.[22]

Results and Discussion

Molecular recognition ability of optically active compounds

Table 1 shows the molecular circular dichroisms (Δε) of the first fractions of $Co(acac)_3$ eluted from the sol–gel and impregnated L-tartaric acid–SiO_2 (sol–gel TA–SiO_2, impregnated TA–SiO_2) columns with *n*-hexane–benzene. L-Tartaric acid alone as a packing agent did not give any resolution. The flow rate varied between <0.005 and 0.3 and increased with increasing L-tartaric acid content in the composites. The flow rate is affected by parameters such as particle size, packing density, affinity, *etc.* Under the present conditions, the particle size and packing conditions of the composites were kept the same. However, the composite particles which contain larger amounts of tartaric acid can be swelled by soaking of the eluent because their silica skeletons are looser and more flexible. This decreases the packing density and increases the flow rate. Another contribution may arise from the affinity between the composite surface and eluent. Here, it is unknown whether micropores of the silica support containing organic matter contribute to the flow rate or not. In the case of impregnated TA–SiO_2, only the composites with L-tartaric acid/SiO_2 ratios of 0.33 (sample I2) and 0.67 (sample I4) gave fractions with low optical activity. It was difficult to resolve the racemate of $Co(acac)_3$ using composites with higher L-tartaric acid content (L-tartaric acid/$SiO_2 \geqslant 1$), even when the flow rate of the eluent was low. On the other hand, with sol–gel TA–SiO_2, fractions with high optical activity were obtained. Although the values seem to oscillate around a plateau, the Δε values of the fractions eluted from the S1–S6 composites were all >50 dm^3 mol^{-1} cm^{-1}. The optical activity of the fractions rapidly decreased upon further increasing the L-tartaric acid content in the composites. These results clearly show that sol–gel TA–SiO_2 composites have a higher recognition abilities than L-tartaric acid itself or impregnated TA–SiO_2 composites towards chiral $Co(acac)_3$. Thus if appropriate amounts of L-tartaric acid and silica are combined by the sol–gel technique, a high synergistic effect appears in chiral recognition. A 1400 mm column of the sol–gel TA–SiO_2 (L-tartaric acid/$SiO_2 = 0.33$) was prepared in order to measure the recognition ability of the sol–gel composite. In the case of $Co(acac)_3$, Δε of the first fraction obtained was -8.6 dm^3 mol^{-1} cm^{-1} at 571 nm. Although the Δε value of optically pure $Co(acac)_3$ is still unknown, the highest Δε value reported so far is *ca.* 6 at 571 nm.[23,24] However, when $Cr(acac)_3$ was used instead of $Co(acac)_3$, the first fraction eluted from the 1400 mm column exhibited $\Delta\varepsilon = -4.4$ dm^3 mol^{-1} cm^{-1} at 535 nm, which corresponds to the value of the optically pure $(+)_{589}$-$Cr(acac)_3$.[25,26] It can be concluded that sol–gel L-TA–SiO_2 composites show a very good recognition ability for the chirality of tris(pentane-2,4-dionato)metal complexes. Fig. 1 shows CD spectra of fractions of $Co(acac)_3$ eluted from the columns packed with sol–gel TA–SiO_2 (L-tartaric acid/$SiO_2 = 0.67$). Spectra a_1 and a_F show CD patterns characteristic of Δ- and Λ-$Co(acac)_3$, respectively.[23,24] Accordingly L-tartaric acid on SiO_2 is found to interact more strongly with the Λ configuration of the $Co(acac)_3$ than with the Δ configuration. Although not shown here, a D-tartaric acid–silica composite column eluted Λ-$Co(acac)_3$ first.

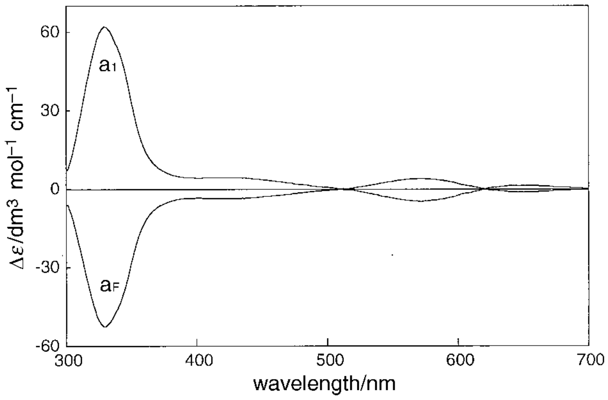

Fig. 1 CD spectra of $Co(acac)_3$ eluted from the sol–gel TA–SiO_2 composite with TA/$SiO_2 = 0.67$. a_1, first fraction by 400 mm column; a_F, final fraction by 400 mm column.

The sol–gel TA–SiO_2 composites prepared with 0.2–0.6 mol tartaric acid (S2–S6) exhibited almost same recognition ability despite the increased tartaric acid content. It is possible that the excess tartaric acid does not contribute to the chiral

Table 1 Effect of the L-tartaric acid content in unwashed L-tartaric acid–silica composites on optical resolution of $Co(acac)_3$ by the composites

sample	L-tartaric acid/SiO_2 (mol/mol)	flow rate/ ml min^{-1}	Δε/dm^3 mol^{-1} cm^{-1} 328 nm	571 nm
L-tartaric acid		0.298	no resolution	
sol–gel TA–SiO_2				
S1	0.1/0.6	very slow	no elution	
S2	0.2/0.6	0.005	58.5	−4.7
S3	0.3/0.6	0.021	50.6	−4.1
S4	0.4/0.6	0.022	61.7	−4.9
S5	0.5/0.6	0.044	64.3	−5.3
S6	0.6/0.6	0.042	61.8	−5.0
S7	0.7/0.6	0.098	28.7	−2.3
S8	0.8/0.6	0.270	4.9	−1.7
impregnated TA–SiO_2				
I1	0.1/0.6	very slow	no elution	
I2	0.2/0.6	0.063	13.7	−1.0
I4	0.4/0.6	0.076	4.9	—
I6	0.6/0.6	0.110	no resolution	
I8	0.8/0.6	0.036	no resolution	

Table 2 Effect of the L-tartaric acid content in washed L-tartaric acid–silica composites on optical resolution of $Co(acac)_3$ by the composites

sample	corresponding unwashed composites (L-tartaric acid/SiO_2)	flow rate/ ml min^{-1}	$\Delta\varepsilon$/dm^3 mol^{-1} cm^{-1} 328 nm	$\Delta\varepsilon$/dm^3 mol^{-1} cm^{-1} 571 nm
WS2	S2 (0.2/0.6)	0.019	92.1	−7.4
WS3	S3 (0.3/0.6)	0.013	89.3	−7.0
WS4	S4 (0.4/0.6)	0.019	21.7	−1.8
WS5	S5 (0.5/0.6)	0.022	39.5	−3.1
WS6	S6 (0.6/0.6)	0.080	29.0	−2.6
WS7	S7 (0.7/0.6)	0.045	17.9	−1.6
WS8	S8 (0.8/0.6)	0.330	no resolution	

recognition ability. Accordingly, to remove the excess L-tartaric acid, the composites were washed as described below and the molecular recognition ability was remeasured. The composites were vigorously stirred in excess *n*-hexane–benzene (1 : 1, v/v) solution for 3 h, then filtered off and dried. A small amount of L-tartaric acid and its diethyl ester were detected in the filtrate. Table 2 shows $\Delta\varepsilon$ of the first fraction of $Co(acac)_3$ eluted from 400 mm columns packed with the washed sol–gel TA–SiO_2. The samples WS2 and WS3 gave higher $\Delta\varepsilon$ values than the corresponding unwashed composites, while the other washed composites showed lower values. Thus, the recognition ability of the composites containing a small amount of tartaric acid increased upon washing. The other composites showed a decrease in their recognition ability after treatment. Some L-tartaric acid molecules in the composite were liberated from the composite during treatment and aggregated to form crystals. The decrease in recognition ability was considered to be due to this formation of crystals on the surface of the composites. The reasons why these changes occurred will be described below.

XRD and TG–DTA studies of composites

Fig. 2 shows the X-ray diffraction patterns of the impregnated TA–SiO_2 composites and pure L-tartaric acid as a reference. All impregnated TA–SiO_2 composites listed in Table 1 showed XRD patterns characteristic of L-tartaric acid crystals and their DTA curves (Fig. 3) showed an endothermic peak around 175 °C corresponding to the melting point of L-tartaric acid. In addition, with increasing L-tartaric acid content in the composites, the diffraction and endothermic intensities of the XRD and DTA profiles became stronger. These results indicate that, in the impregnated TA–SiO_2 composites, L-tartaric acid molecules readily aggregate and are dispersed as crystals. The TEOS derived silica gel used for the preparation of impregnated TA–SiO_2 composites also exhibited a mass loss and exothermic peak around 350 °C which corresponds to the decomposition of unhydrolysed ethoxy groups remaining in the gel as seen in the DTA curves of Fig. 3(a)–(c). On the other hand, curves (d) and (e) show no exothermic peak around 350 °C but instead a broad peak around 250 °C. These facts suggest that the unhydrolysed ethoxy groups were released during the impregnation when the impregnated L-tartaric acid content was high. However, these unhydrolysed ethoxy groups seem to play an important role in the recognition. Neither impregnated TA–SiO_2 composites prepared using commercial silica gel for chromatography (Nakarai, Silica gel No. 1) as a support nor composites prepared by using sol–gel derived silica gel calcined at 500 °C (containing no organics) exhibited any molecular recognition ability, regardless of the L-tartaric acid content. Although details of the role of the remaining ethoxy groups are unknown, it is expected that they are substituted by L-tartaric acid leading to fixing of the latter on the silica surface [eqn. (1), R = CH(OH)CH(OH)COOH]

$$\equiv Si-O-C_2H_5 + HOOCR \rightarrow \equiv Si-O-OCR + C_2H_5OH \qquad (1)$$

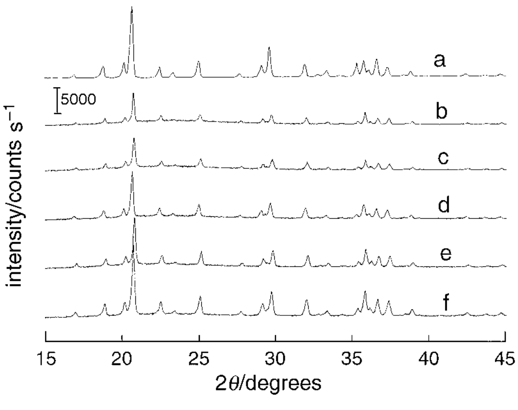

Fig. 2 XRD patterns of impregnation TA–SiO_2 composites and pure L-tartaric acid. (a) L-Tartaric acid, (b) I1 (TA/SiO_2 = 0.17), (c) I2 (TA/SiO_2 = 0.33), (d) I4 (TA/SiO_2 = 0.67), (e) I6 (TA/SiO_2 = 1.00), (f) I8 (TA/SiO_2 = 1.33).

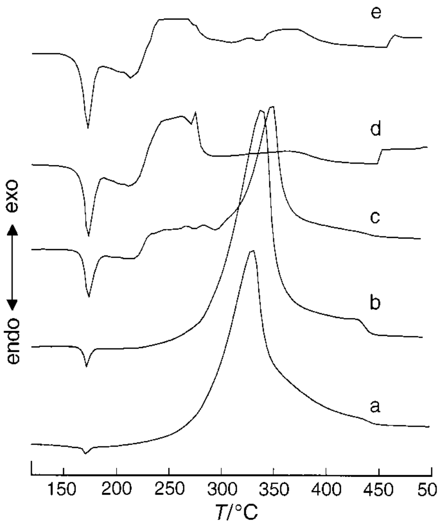

Fig. 3 DTA curves of impregnation TA–SiO_2 composites. (a) I1 (TA/SiO_2 = 0.17), (b) I2 (TA/SiO_2 = 0.33), (c) I4 (TA/SiO_2 = 0.67), (d) I6 (TA/SiO_2 = 1.00), (e) I8 (TA/SiO_2 = 1.33).

On the other hand, all sol–gel TA–SiO_2 composites exhibited neither clear XRD patterns of a crystalline phase nor an endothermic peak around 175 °C (melting point of L-tartaric acid) in their DTA curves. This suggests that, although the composites certainly contain a large amount of L-tartaric acid, this does not exist in a crystalline form and is highly dispersed. The above substitution reaction is also probable during the preparation of sol–gel composites, but in this case L-tartaric acid molecules exist not only on the silica surface but also within the silica matrix. Another possibility is that L-tartaric acid reacts with ethanol or propan-2-ol to form esters such as L-tartaric acid diethyl ester which are difficult to crystallize at room temperature. Such an esterification would only partially proceed; however, a greater portion of the L-tartaric acid should exist unchanged. The XRD peaks attributable to L-tartaric acid became stronger when the composites were washed repeatedly (Fig. 4) yet L-tartaric acid diethyl ester is not easily hydrolysed to L-tartaric acid by simply washing at room temperature.

The washed composites WS5–WS8 exhibited weak XRD peaks attributable to crystalline L-tartaric acid. This means that some tartaric acid dispersed in the silica matrix was liberated and crystallized during the washing treatment. Since L-tartaric acid crystals themselves have no recognition ability, it can be deduced that these composites lost their high molecular recognition ability due to the precipitation of L-tartaric

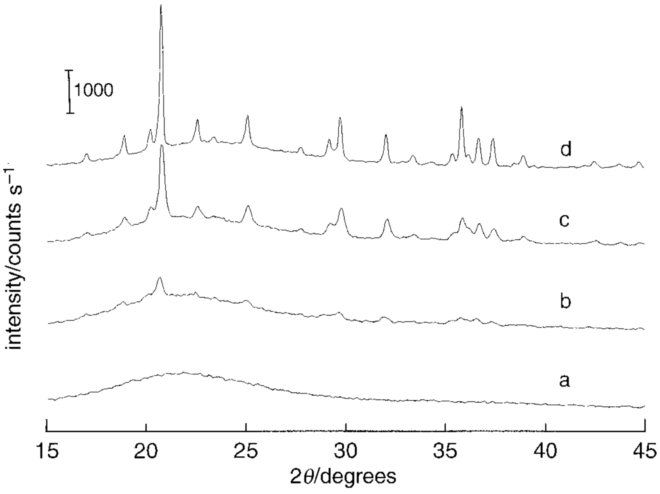

Fig. 4 XRD patterns of sol–gel TA–SiO_2 composite S7 (TA/SiO_2 = 1.17) washed repeatedly. (a) No wash, S7, (b) after one wash, WS7, (c) after two washes, (d) after three washes.

acid crystals on the surface of the composites. In contrast, XRD patterns of WS2 and WS3, whose molecular recognition abilities were increased upon washing, were unaltered with no peaks attributable to L-tartaric acid being detected. If we assume that weakly adsorbed or simply dispersed L-tartaric acid was liberated from the composite during the washing and, once liberated, molecules were crystallized on the surface of the composite in the drying process, the decrease in the molecular recognition ability of the composites can be easily understood. The amount of liberated L-tartaric acid should increase as the L-tartaric acid content in the composites increases. On the other hand, the increase in the recognition ability observed on the SW2 and SW3 would be due to the removal of redundant L-tartaric acid crystals.

IR and NMR studies on gel formation

The molecular recognition ability of the sol–gel composites seems to be determined by L-tartaric acid dispersed in the silica matrix in non-crystalline form, probably as isolated molecules. We investigated this condensation process by IR and NMR spectroscopy in order to examine how the silicon coordination sphere changed when L-tartaric acid and water were added. Then the chemical state of L-tartaric acid which is highly dispersed in the composite was investigated. Fig. 5 shows the IR spectra of pure $Si(OEt)_4$ (a), L-tartaric acid (b) and silica gel derived from TEOS (c). Spectrum (a) exhibits sharp bands at 2960, 2930, 2870 cm^{-1} and 1460, 1380 cm^{-1} corresponding to the stretching and bending vibrations of the aliphatic CH_2 and CH_3 groups, respectively. Two bands can also be seen at low wavenumber, around 1100 cm^{-1}, corresponding to the Si—O—R stretching vibrations of ethoxy groups directly bonded to silicon.[27] Spectrum (b) shows characteristic bands at 1740 cm^{-1} for the C=O stretch and 3200–3600 cm^{-1} for O—H stretch and hydrogen bonded O—H. Calcined silica gel derived from TEOS [Fig. 5(c)] exhibits absorption bands typical for silica as reported in the literature.[28] Fig. 6 shows the IR spectra of the clear viscous solutions obtained after adding 0.2 mol (a) and 0.6 mol (b) of L-tartaric acid to 0.6 mol of TEOS and reacting at 80 °C for 2 h. In both spectra, the above-mentioned bands which are typical of organic groups and Si—O—R bonds were still observed together with new bands corresponding to silica gel. This indicates that hydrolysis–condensation reactions have already partially occurred before the addition of water regardless of the L-tartaric acid content. A small amount of water contained in the solvent or formed by the esterification reaction between tartaric acid and alcohol would cause the hydrolysis–condensation reactions since TEOS molecules are easily and rapidly hydrolysed under acidic conditions in the presence of even small amounts of water.[29] Fig. 7 shows the IR spectra of dried and washed composites and showed IR spectra similar to spectra obtained before the addition of hydrolysis water. The only difference was in the characteristic bands of ethoxy groups around 3000 cm^{-1} which became weaker with washing. Only the washed gel prepared with TA/TEOS = 0.6/0.6 (sample WS6), which showed XRD peaks attributable to L-tartaric acid crystals, gave two absorption peaks around 3400 cm^{-1}. These are attributable to hydrogen bonds typically observed

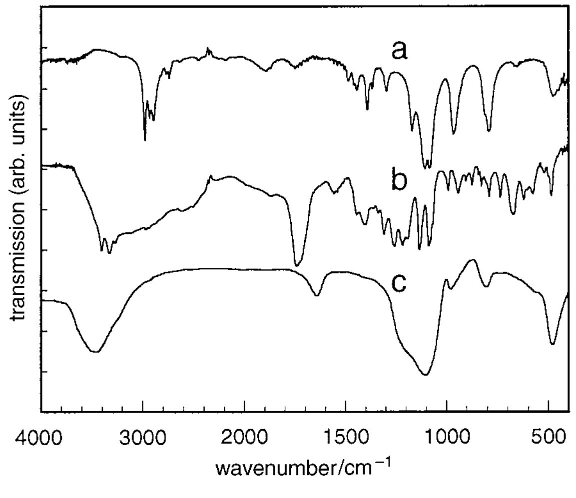

Fig. 5 IR spectra of TEOS (a), L-tartaric acid (b) and calcined silica gel derived from TEOS (c)

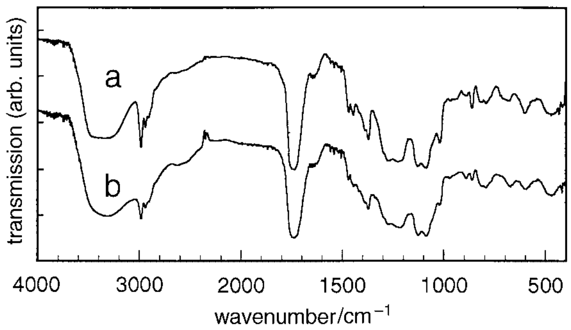

Fig. 6 IR spectra of the clear viscous solution obtained after adding 0.2 mol (a) and 0.6 mol (b) of L-tartaric acid to 0.6 mol of TEOS and reacting at 80 °C for 2 h

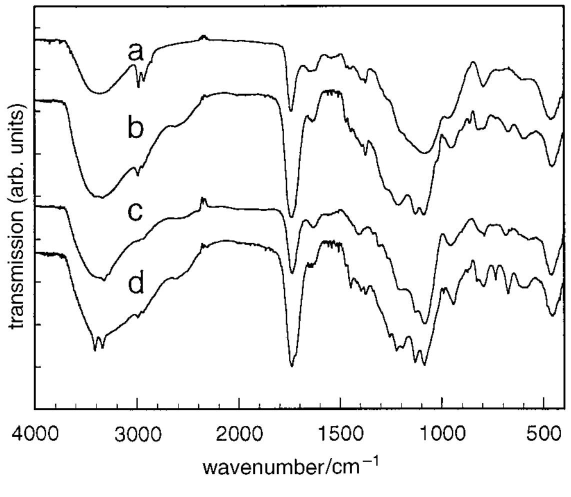

Fig. 7 IR spectra of sol–gel TA–SiO_2 composites and washed sol–gel TA–SiO_2 composites. (a) S2 (TA/SiO_2 = 0.33), (b) S6 (TA/SiO_2 = 1.00), (c) WS2 (TA/SiO_2 = 0.33), (d) WS6 (TA/SiO_2 = 1.00).

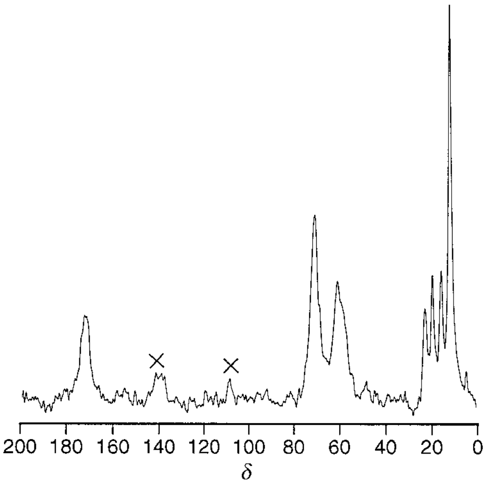

Fig. 8 ^{13}C CP MAS NMR spectrum of the sol–gel TA–SiO$_2$ (S2) (×, spinning side band)

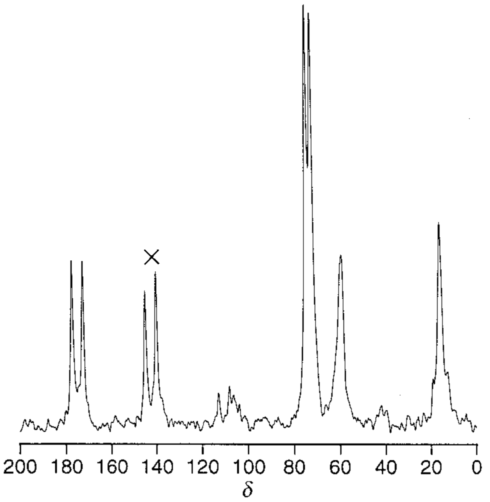

Fig. 9 ^{13}C CP MAS NMR spectrum of impregnation TA–SiO$_2$ composites (I2) (×, spinning side band)

in L-tartaric acid crystals whose structure is built up of a three-dimensional network of O—H—O hydrogen bonds.[30]

Fig. 8 and 9 show ^{13}C CP MAS NMR spectra of sol–gel TA–SiO$_2$ (S2) and impregnated TA–SiO$_2$ composites (I2), respectively. The former gives peaks at around 172 (172.99, 172.00) and 72.33 ppm assigned to the carbonyl and α-carbon of L-tartaric acid, together with peaks attributable to $-O\underline{C}H_2CH_3$, $-OCH_2\underline{C}H_3$ and $-CH(\underline{C}H_3)_2$ derived from ethanol, ethoxy groups and propan-2-ol. The strong peaks derived from the ethoxy group (13.69 ppm for $-OCH_2\underline{C}H_3$ and 62.56 ppm for $-O\underline{C}H_2CH_3$) indicate that the composite contains a significant amount of unhydrolysed ethoxy groups as well as L-tartaric acid. The latter, however, exhibits two carbonyl (176.20, 171.41 ppm) and two α-carbon (74.07, 71.84 ppm) resonances. According to the literature,[31] crystalline tartaric acid gives two doublet resonance peaks since the carbonyl and α-carbon atoms within a single acid molecule are not equivalent. Since the composites prepared by the impregnation method contain L-tartaric acid crystals, two doublet resonances should be observed. On the other hand, the chemical shifts of carbonyl and α-carbon of L-tartaric acid in the sol–gel composite were different from those of L-tartaric acid in aqueous solution (175.3, 72.8 ppm).[32] In particular, the chemical shift of the carboxyl carbon was shifted to low magnetic field, suggesting the presence of ester groups such as $-COO-C\equiv$ or $-COO-Si\equiv$. The chemical shift of the carboxyl carbon in L-tartaric acid diethyl ester appeared at 171.98 ppm, so the peak at 172.99 ppm or the shoulder of this broad peak could correspond to carboxylic groups bonded to silicon atoms. Similar results were obtained with the other sol–gel composites although the resonance peak at around 172 ppm was sometimes broad and not resolved into two peaks. ^{29}Si MAS NMR spectra of the sol–gel TA–SiO$_2$ (S5) at various preparation stages are displayed in Fig. 10. The peaks at around −95, −102 and −110 ppm can be assigned to middle (Q^2), branching (Q^3), and cross-linking (Q^4) siloxane skeletal species according to literature data.[33] The spectrum of Fig. 10(a), a reaction mixture of TEOS, tartaric acid and solvent, showed Q^2 and Q^3 peaks suggesting that the hydrolysis–condensation reactions occurred before the addition of water as also observed in the IR measurement. As the reaction proceeded the Q^2 peak reduced in intensity as the Q^4 peak grew. However, the spectrum of the dried gel (c) still showed

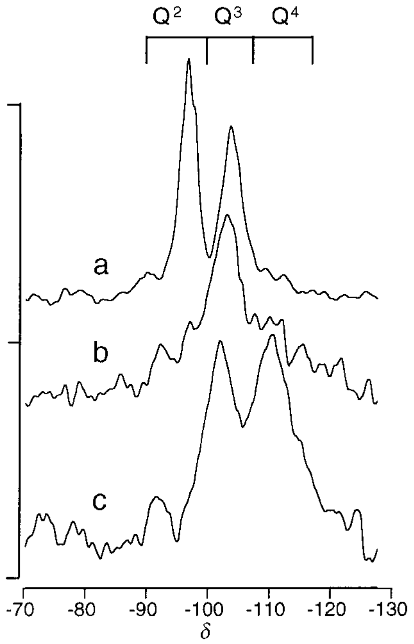

Fig. 10 ^{29}Si CP MAS NMR spectrum of the sol–gel TA–SiO$_2$ (S5). (a) Before the addition of hydrolysis water, (b) just after gelation (2 h after the addition of hydrolysis water), (c) after ageing and drying.

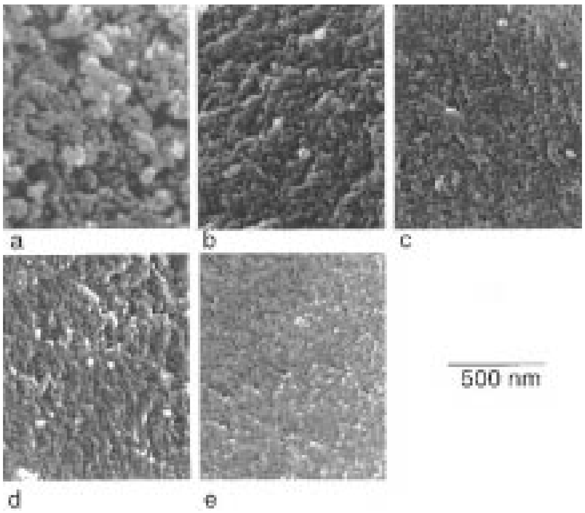

Fig. 11 SEM images of the calcined sol–gel composites and the support gel used for impregnation composites. (a) S1 (TA/SiO$_2$=0.17), (b) S3 (TA/SiO$_2$=0.50), (c) S5 (TA/SiO$_2$=0.83), (d) S7 (TA/SiO$_2$=1.17), (e) I (TA/SiO$_2$=0, support for impregnation composites).

a Q^3 peak suggesting the existence of silicon atoms bonded to hydroxy or ethoxy groups or tartaric acid. The other sol–gel composites showed similar spectra. As the above results suggest, assuming that the substitution reaction between the ethoxy groups of TEOS and carboxylic groups of the L-tartaric acid occurred, a high dispersion of L-tartaric acid in the sol–gel composites would result. Livage and co-workers have studied the modification of alkoxide precursors[34–36] and confirmed from both IR and NMR experiments that acetic acid can bond to both hydrolysed and non-hydrolysed TEOS as a monodentate ligand.[36] It is doubtful, however, if all the acetic acid molecules have bonded to silicon atoms. In the case of L-tartaric acid and TEOS, NMR results suggest the presence of L-tartaric acid bonded to silicon atoms, but the coordination state of L-tartaric acid, proportion of tartaric acid bonding to silicon and state of non-bonding L-tartaric acid in the composite have not been clarified.

Structure of silica support

The properties of the alkoxide derived silica gels, including the morphological structure, changed depending on preparation conditions such as pH,[37,38] temperature[39] and solvent used.[40] Therefore it is worth investigating the properties of the silica gel supports used in the present study. All samples were calcined at 450 °C to remove organics present in the composites before the measurements. Fig. 11 shows the SEM images of silica supports after calcination. All the silica gels were essentially composed of small particles with diameters <30 nm and their size decreased as the L-tartaric acid content in the composite was increased. These particles aggregate and form secondary particles in the micrometre range. N_2 adsorption and desorption isotherms of representative samples and calculated pore size distribution curves are shown in Fig. 12 and 13, respectively. The shape of the isotherms changed with the amounts of tartaric acid added in the preparation. All the adsorption isotherms of the calcined silica samples exhibited a sharp knee at low relative pressures suggesting the existence of micropores. Except for the calcined S1 and S2 samples which exhibited type II isotherms, the adsorption isotherms of the other samples were basically of type IV, typically observed for mesoporous solids, in the classification by Brunauer, Deming, Deming and Teller (BDDT).[41] Accordingly, the silicas are expected to have both micropores <2 nm in diameter and larger pores. All the silicas have pores with radii in the range 1–50 nm as can be seen in Fig. 12. Further, the silicas prepared with small amounts of L-tartaric acid showed pore size distributions in the larger size range while those prepared with larger amounts of L-tartaric acid gave rather sharp distributions in the nanometre range. The calcined silica gel support used for impregnated composites did not show an obvious pore size distribution peak in the range 1–100 nm. Table 3 lists the BET surface area (S_{BET}), external surface area (S_{ex}) derived from meso- and macro-pores, and pore volume (V_p) of the calcined silicas. S_{BET} values increased significantly upon increasing the amount of tartaric acid used; however, the difference in the total pore volume between the silicas was rather small. It is considered that the increase in S_{BET} is attributable to an increase in the number micropores which can be formed by burning of the organics[17,42,43] because the composites contain significant quantities of tartaric acid and unhydrolysed ethoxy groups. Such micropores filled with

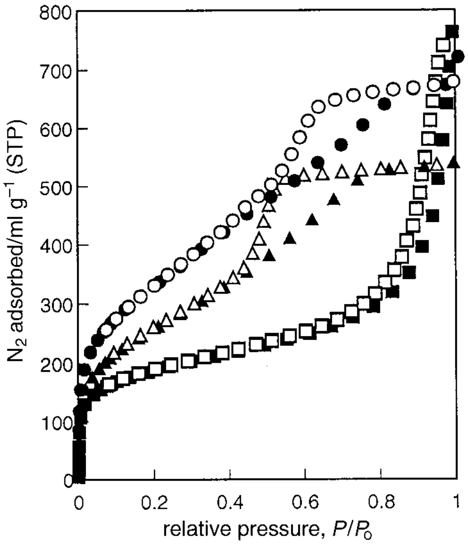

Fig. 12 N_2 adsorption and desorption isotherms of the calcined sol–gel composites. (■□) S1 ($TA/SiO_2=0.17$), (▲△) S4 ($TA/SiO_2=0.67$), (●○) S7 ($TA/SiO_2=1.17$). Solid symbols, adsorption; open symbols, desorption.

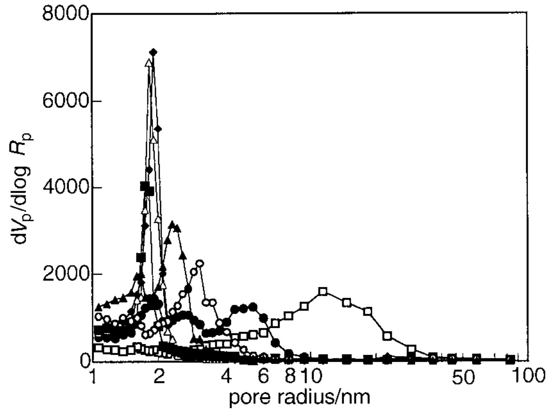

Fig. 13 Pore size distributions of the calcined sol–gel composites. (□) S1 ($TA/SiO_2=0.17$), (●) S2 ($TA/SiO_2=0.33$), (△) S3 ($TA/SiO_2=0.50$), (◆) S4 ($TA/SiO_2=0.67$), (■) S5 ($TA/SiO_2=0.83$), (○) S6 ($TA/SiO_2=1.00$), (▲) S7 ($TA/SiO_2=1.17$).

Table 3 S_{BET}, S_{ex} and V_p of the silica gels prepared by calcination[a] of the composites

			V_p/ml g^{-1}			
sample	S_{BET}/m^2 g^{-1}	S_{ex}/m^2 g^{-1}	total	<2 nm[b]	2–50 nm	>50 nm
S1	687	304	1.17	0.30	0.51	0.36
S2	847	342	0.95	0.35	0.56	0.04
S3	933	25	0.80	0.37	0.41	0.02
S4	994	17	0.84	0.38	0.45	0.01
S5	1062	32	0.79	0.43	0.31	0.05
S6	1087	153	0.97	0.44	0.51	0.02
S7	1220	87	1.08	0.49	0.55	0.04
S8	1175	41	0.81	0.48	0.33	<0.01
I[c]	298	2	0.17	0.14	0.01	0.02

[a] 450 °C for 3 h in air to remove organics. [b] Diameter of pore. [c] Silica gel used for impregnated composites calcined before impregnation.

organics would not be effective for recognition. Concerning the volumes of larger pores and external surfaces, no remarkable features which may explain the high recognition ability of the composites S2–S6 were perceived. Considering the ease of access, external and pore surfaces in the vicinity of the outer surface on which tartaric acid molecules are highly dispersed would be active for recognition regardless of the microporosity, total surface area and amounts of tartaric acid existing in the micropores inside the matrix.

Conclusions

L-Tartaric acid–silica composites prepared by the sol–gel process showed high optical resolution ability for tris(pentane-2,4-dionato)metal complexes. The sol–gel composites contain highly dispersed L-tartaric acid in non-crystalline form while the composites prepared by a conventional impregnation method contain crystalline L-tartaric acid. NMR measurements suggest the presence of substituted L-tartaric acid. By such substitution, L-tartaric acid molecules fixed or adsorbed on the silica matrix can be highly dispersed. On the other hand, the silica gel supports were aggregates composed of small particles with diameters <30 nm. The supports have rugged surfaces which give a large surface area available to interact with molecules. Thus, the molecular recognition ability of the composites was deduced to arise from the combined effect of the silica support and the highly dispersed optically active compound. The sol–gel procedure is suitable for realizing the potential of optically active organic compounds for chiral recognition or certain combined effects of organic and inorganic compounds (*e.g.* the synergism of silica and L-tartaric acid).

References

1 H. R. Allcock, *Adv. Mater.*, 1994, **6**, 106.
2 H. E. Lee and H. W. Jarrett, *J. Chromatogr.*, 1990, **511**, 69.
3 F. Gasparrini, D. Misiti, C. Villani, F. La Torre and M. Sinibaldi, *J. Chromatogr. A*, 1988, **457**, 235.
4 S. Oi, M. Shijo and S. Miyano, *Chem. Lett.*, 1990, 59.
5 W. H. Pirkle and T. C. Pochapsky, *J. Am. Chem. Soc.*, 1986, **108**, 352.
6 Y. Dobashi and S. Hara, *J. Org. Chem.*, 1987, **52**, 2490.
7 S. Oi, M. Shijo, Y. Yamashita and S. Miyano, *Chem. Lett.*, 1988, 1545.
8 G. Blaschke, W. Bröker and W. Frankel, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 830.
9 P. Roumeliotis, A. A. Kurbanov and V. A. Davankov, *J. Chromatogr.*, 1983, **266**, 439.
10 Y. Okamoto, S. Honda, I. Okamoto and H. Yuki, *J. Am. Chem. Soc.*, 1981, **103**, 6971.
11 T. Shibata, I. Okamoto and K. Ishii, *J. Liq. Chromatogr.*, 1986, **9**, 313.
12 Y. Okamoto, M. Kawashima, K. Yamamoto and K. Hatada, *Chem. Lett.*, 1984, 739.
13 T. Shibata, T. Sei, H. Nishimura and K. Deguchi, *Chromatographia*, 1987, **24**, 552.
14 Y. Okamoto, R. Aburatani, T. Fukumoto and K. Hatada, *Chem. Lett.*, 1987, 1857.
15 F. Mizukami, S. Niwa, S. Ohkawa and A. Katayama, *Stud. Surf. Sci. Catal.*, 1993, **78**, 337.
16 K. Maeda, F. Mizukami, M. Watanabe, S. Niwa, M. Toba and K. Shimizu, *Chem. Ind.*, 1989, 807.
17 M. Toba, F. Mizukami, S. Niwa and K. Maeda, *J. Chem. Soc., Chem. Commun.*, 1990, 1211.
18 S. Niwa, F. Mizukami, S. Isoyama, T. Tsuchiya, K. Shimizu, S. Imai and J. Imamura, *J. Chem. Tech. Biotechnol.*, 1986, **36**, 236.
19 G. Zehl, S. Bischoff, F. Mizukami, H. Izutsu, M. Bartoszek, H. Jancke, B. Lucke and K. Maeda, *J. Mater. Chem.*, 1995, **5**, 1893.
20 F. Mizukami, H. Izutsu, T. Osaka, Y. Akiyama, N. Uiji, K. Moriya, K. Endo, K. Maeda, Y. Kiyozumi and K. Sakaguchi, *J. Chromatogr. A*, 1995, **697**, 279.
21 D. Dollimore and G. R. Heal, *J. Appl. Chem.*, 1964, **14**, 109.
22 R. S. Mikhail, S. Brunauer and E. E. Boder, *J. Colloid Interface Sci.*, 1968, **26**, 45.
23 R. B. Von Dreele and R. C. Fay, *J. Am. Chem. Soc.*, 1971, **93**, 4936.
24 R. C. Fay, A. Y. Girgis and U. Klabunde, *J. Am. Chem. Soc.*, 1970, **92**, 7075.
25 H. Yoneda, U. Sakaguchi and Y. Nakashima, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 1200.
26 K. L. Stevenson, *J. Am. Chem. Soc.*, 1972, **94**, 6652.
27 A. L. Smith, *Spectrochim. Acta*, 1960, **16**, 87.
28 D. L. Wood and E. M. Rabinovich, *Appl. Spectrosc.*, 1989, **43**, 263.
29 M. Yamane, S. Inoue and A. Yasumori, *J. Non-Cryst. Solids*, 1984, **63**, 13.
30 Y. Okaya and N. R. Stemple, *Acta Crystallogr.*, 1966, **21**, 237.
31 H. D. W. Hill, A. P. Zens and J. Jacobus, *J. Am. Chem. Soc.*, 1979, **101**, 7090.
32 J. F. Johnson and W. C. Jakowski, *Carbon-13 NMR Spectra*, Wiley, New York, 1972, p. 64.
33 E. Lippmaa, M. Mägi, A. Samoson, G. Engelhardt and A-R. Grimmer, *J. Am. Chem. Soc.*, 1980, **102**, 4889.
34 S. Doeuff, M. Henry, C. Sanchez and J. Livage, *J. Non-Cryst. Solids*, 1987, **89**, 206.
35 C. Sanchez, J. Livage, M. Henry and F. Babonneau, *J. Non-Cryst. Solids*, 1988, **100**, 65.
36 A. Campero, R. Arroyo, C. Sanchez and J. Livage, in *Ultrastructure Processing of Advanced Ceramics*, ed. J. D. Mackenzie and D. R. Ulrich, Wiley, New York, 1987, p. 327.
37 R. K. Iler, in *The Chemistry of Silica*, Wiley, New York, 1979, p. 174.
38 J. C. Ro and I. J. Chung, *J. Non-Cryst. Solids*, 1991, **130**, 8.
39 M. W. Colby, A. Osaka and J. D. Mackenzie, *J. Non-Cryst. Solids*, 1986, **82**, 37.
40 T. Latagiri and Y. Maekawa, *J. Non-Cryst. Solids*, 1991, **134**, 183.
41 S. Brunauer, L. S. Deming, W. E. Deming and E. Teller, *J. Am. Chem. Soc.*, 1940, **62**, 1723.
42 Y. Chujo, *Kagaku*, 1993, **48**, 647.
43 Y. Chujo and T. Saegusa, *Adv. Polym. Sci.*, 1992, **100**, 11.

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