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Hydrothermal synthesis and characterization of alkali metal titanium silicates†

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Preparation of granulated alkali metal titanium silicates is described in which the desired silicon to titanium ratio is controlled *via* a sol–gel route, using hexamethylenetetramine as an inner gelation reagent. The amorphous precursors are treated hydrothermally in the presence of NaOH or KOH solution under mild conditions (150–250 °C). By varying the Si:Ti molar ratio in the precursor, concentration of alkali, temperature and duration of treatment, six granular sodium titanium silicates ($Na_2Ti_2O_3SiO_4{\cdot}2H_2O$, $Na_2TiSi_2O_7{\cdot}2H_2O$, $Na_2TiOSiO_4$ and three novel phases characterized by the first reflection in the XRD at 10.8, 7.2 and 5.4 Å, respectively) and two potassium titanium silicates [$K_3H(TiO)_4(SiO_4)_3{\cdot}8H_2O$, $K_2TiSi_3O_9{\cdot}H_2O$] were synthesized. All compounds were characterized by elemental analysis, TGA, powder XRD, SEM and ^{29}Si MAS NMR spectroscopy. Some of the titanium silicates are thermally stable, possessing unique ion exchange properties for alkali, alkaline earth, and some toxic heavy metal cations.

Introduction

Alkali metal titanium silicates have received considerable attention in the recent past.[1–7] This is because some, like ETS-4 or ETS-10,[3–5] form frameworks analogous to those existing in zeolites, whereas others, like $Na_2Ti_2O_3(SiO_4){\cdot}H_2O$[6,8] or $K_2TiSi_3O_9{\cdot}H_2O$,[9] have tunnels or channels containing exchangeable ions. Thus, they form members of an ever expanding family of inorganic framework structures and ion exchangers, that makes them extremely attractive for catalytic applications, molecular and ion sieving and selective ion separations due to their high thermal, chemical (in acid and alkaline media) and radiation stability and resistance to oxidation. However, alkali metal titanium silicates, with the exception of ETS-4 and ETS-10, have not yet found wide application. The main reason for this is related to technical problems over their preparation in granulated form acceptable for industrial usage.

We report here our preliminary data on the possible preparation of some metastable alkali metal titanium silicates in granular form *via* hydrothermal treatment of amorphous, granulated, titanium silicate precursors.

Experimental

Reagents

All reagents were of analytical grade (Aldrich) and were used without further purification.

Analytical procedures

The diffractometer used was a Seifert-Scintag PAD-V with Cu-Kα radiation. Titanium, silicon, sodium and potassium content in the solids was determined using a SpectraSpec Spectrometer DCP-AEC. IR spectra were obtained on a Perkin-Elmer 1720-X FT spectrophotometer by the KBr pellet technique. ^{29}Si NMR spectra at magic angle were obtained on a Bruker MSL-300 spectrometer. Electron micrographs were recorded with a JEOL JSM 6100 electron microscope operating at 20 kV.

Ion exchange study

The affinity of the titanium silicates towards the ions of interest was studied in individual 10^{-3} M MCl_n aqueous solutions ($M = Li^+$, Na^+, K^+, Cs^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Cu^{2+} or Co^{2+}; $n = 1,2$) or in the presence of background electrolytes at $V{:}m = 200{:}1$ (mL g^{-1}), pH 7–9 and 25 °C. In all cases, contact time was 5 days. The pH of solutions after equilibration with the adsorbent was measured using a Corning-340 pH meter. Final concentrations of all the cations in solution were measured using a Varian SpectrAA-300 atomic absorption spectrometer. The affinity of the titanium silicates towards the elements of interest was expressed through the distribution coefficient (K_d, mL g^{-1}) values calculated from the formula $K_d = [(c_o - c_i)/c_i]{\cdot}(V/m)$, where c_o and c_i are the ion concentrations in the initial solution and after equilibration with exchanger, respectively, and V/m is the volume to mass ratio.

Preparation of the alkali metal titanium silicates

Several granulated titanium silicate precursors with different Si:Ti molar ratios (from 0.5:1 to 2:1) were prepared *via* the sol–gel method. A titanium and silicon containing solution (solution A) was first prepared by adding a calculated amount of Ludox solution (35–140 mL) to 150 mL of a freshly prepared titanium(IV) chloride solution (containing 48 g of titanium per liter) in 1 M HCl. A neutralizing solution (solution B) was prepared by dissolving 26 g of hexamethylenetetramine, 20 g of urea and 40 mL of 25% NH_3 (aq) in 150 mL of water. Both solutions were cooled to 5 °C before mixing. After that, neutralizing solution B was added dropwise and with vigorous stirring to the Ti–Si containing solution A. The reaction mixture obtained was heated at 60–70 °C to form a homogeneous gel. All gels were aged for 12 h and then dried at either 60 °C or 600 °C.

Granular titanium silicate xerogels (with 0.25–0.5 mm particle size) were used as precursors for one preparation of the crystalline alkali metal titanium silicates. A typical procedure includes hydrothermal treatment of 3 g of precursor

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Table 1 Synthetic conditions for the preparation of the granular alkali metal titanium silicates

Si : Ti Molar ratio in the precursor	Thermal treatment of the precursor/ °C	Alkali concentration/ mol L^{-1}	Phase formed
0.5 : 1	60	1.0 NaOH	7.9 Å
0.5 : 1	60	2.0 NaOH	7.9 Å
0.5 : 1	60	3.0 NaOH	5.1 Å
1 : 1	60	0.5 NaOH	10.8 Å
1 : 1	60	1.0 NaOH	11.8 Å
1 : 1	60	2.0 NaOH	5.1 Å + 7.9 Å
1 : 1	60	3.0 NaOH	5.1 Å
1.5 : 1	60	0.5 NaOH	10.8 Å
1.5 : 1	60	2.0 NaOH	7.9 Å
1.5 : 1	60	3.0 NaOH	5.1 Å
2 : 1	60	1.0 NaOH	amorphous
2 : 1	60	2.0 NaOH	14.9 Å
2 : 1	60	3.0 NaOH	5.1 Å
1 : 1	600	0.5 NaOH	5.4 Å
1.5 : 1	600	1.0 NaOH	7.2 Å
2 : 1	600	2.0 NaOH	11.8 Å
2 : 1	600	3.0 NaOH	7.9 Å
2 : 1	60	2.0 KOH	7.94 Å
2 : 1	60	3.0 KOH	7.8 Å

Sodium titanium silicates: 5.1 Å phase is $Na_2TiOSiO_4$; 7.9 Å phase is $Na_2Ti_2O_3SiO_4 \cdot 2H_2O$; 11.8 Å phase is ETS4; 14.9 Å phase is $Na_2TiSi_2O_7 \cdot 2H_2O$; 5.4 Å, 7.2 and 10.8 Å phases are new. Potassium titanium silicates: 7.8 Å phase is $K_3H(TiO)_4(SiO_4)_3 \cdot 8H_2O$, 7.94 Å phase is $K_2TiSi_3O_9 \cdot H_2O$.

with 30 mL of a 0.5–3 M NaOH (KOH) solution in a 100 mL, Teflon lined autoclave at 180–190 °C and autogeneous pressure for 48 h. The products obtained were separated by filtration, washed with water and dried at 60–70 °C. The synthesis conditions of the titanium silicates are summarized in Table 1.

Results and discussion

According to the data presented in Table 1 the formation of several different sodium and potassium titanium silicates takes place when amorphous titanium silicate precursors are treated hydrothermally in alkaline media. Summarizing, six granular sodium titanium silicates: $Na_2Ti_2O_3SiO_4 \cdot 2H_2O$ (7.9 Å), $Na_2TiSi_2O_7 \cdot 2H_2O$ (14.9 Å), $Na_2TiOSiO_4$ (5.1 Å) and three novel phases characterized by the first reflection in the XRD powder patterns at 10.8, 7.2 and 5.4 Å, respectively, and two potassium titanium silicates: $K_3H(TiO)_4(SiO_4)_3 \cdot 8H_2O$, $K_2TiSi_3O_9 \cdot H_2O$, were synthesized. The positions of their XRD reflections are shown in Table 2. Elemental analysis data for the new compounds, their empirical formulas and the positions of the ^{29}Si MAS NMR peaks are presented in Table 3. The SEM photographs of the three novel sodium titanium silicates

Table 2 The positions of the XRD reflections of the new sodium titanium silicates

10.8 Å phase		7.2 Å phase		5.4 Å phase	
d/Å	*I*(%)	*d*/Å	*I*(%)	*d*/Å	*I*(%)
10.8	73	7.89	5	7.65	7
6.11	2	7.21	55	5.41	100
5.40	100	6.57	84	4.14	20
4.35	13	5.07	19	4.00	52
4.29	3	4.51	11	3.81	59
3.60	44	4.38	11	3.41	98
3.50	7	3.99	16	3.27	91
3.36	16	3.81	5	3.21	28
3.22	6	3.41	6	2.75	12
3.16	5	3.25	100	2.69	11
3.06	1	3.19	39	2.59	45
2.82	1	3.14	26	2.53	69
2.62	1	3.00	8	2.40	15
2.58	6	2.83	5	2.33	16
2.53	2	2.76	13	2.23	5
2.46	1	2.65	22	2.11	8
2.38	2	2.55	28	2.08	5
2.29	1	2.52	26	2.06	11
2.06	9	2.32	4	1.99	14
		2.24	5	1.98	18
		2.16	5	1.94	8
		2.07	3	1.86	6
		1.97	8		

Table 3 Characterization of the new granular alkali metal titanium silicates. The content of elements in the compounds is given in atom%

Phase	Si[a]	Ti	Na	Tentative formula[b]	^{29}Si MAS NMR (ppm)
10.8 Å	10.4	20.5	4.9	$Na_2Ti_8Si_4O_{25} \cdot 5H_2O$	−96.4; −107.3
7.2 Å	12.7	15.2	10.7	$Na_2Ti_3Si_2O_{11} \cdot 2H_2O$	−90.2
5.4 Å	8.2	23.2	3.8	$Na_2Ti_8O_{13}(SiO_4)_2$	−94.2; −96.9

[a] Samples were dissolved in a small amount of HF(aq) to which H_3BO_3 was subsequently added to bind F^-. [b] Water content in the compounds was determined thermogravimetrically.

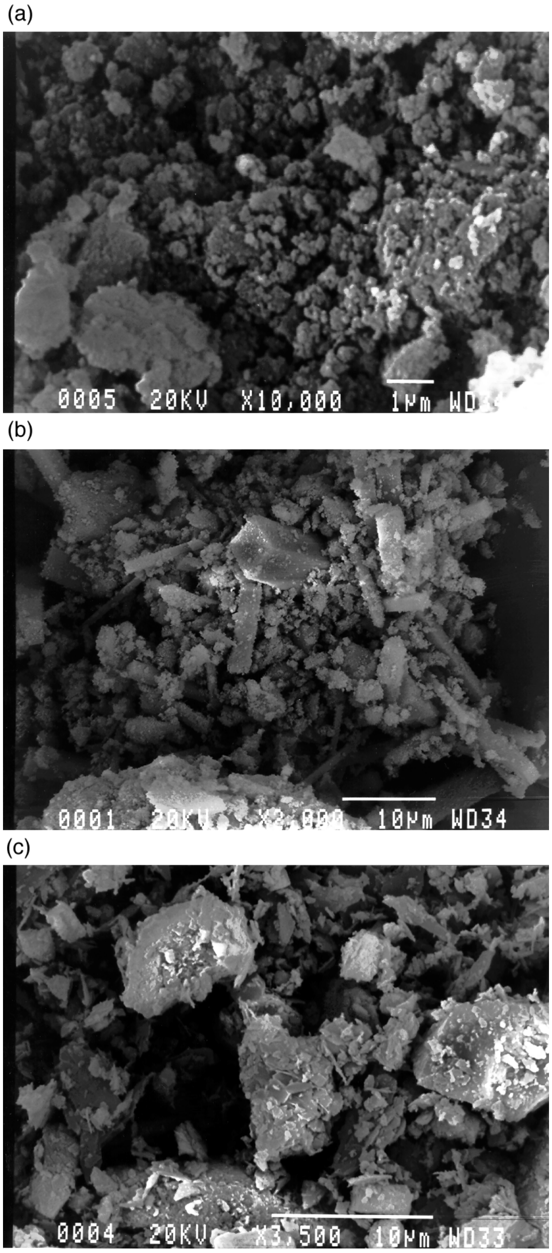

Fig. 1 Scanning electron micrographs showing the morphology of the novel sodium titanium silicate phases: 10.8 Å (a), 5.4 Å (b) and 7.2 Å (c).

Table 4 The K_d values (mL g^{-1}) for metal ion uptake by the granular titanium silicates

	14.9 Å	ETS-4	10.8 Å	7.9 Å	7.2 Å	5.4 Å	7.8 Å (K-form)	7.94 Å (K-form)
Li	400	850	100	950	35,000	10	460	10
K	1,800	5,500	320	8,300	220	15	—	—
Rb	2,400	2,600	580	16,000	1,200	25	10,300	250
Cs	4,500	2,950	370	22,000	220	15	13,000	1,100
Mg	950	670	890	330	280	120	1,200	250
Ca	4,150	6,600	4,100	7,450	4,200	110	4,800	500
Sr	240,000	71,000	46,900	137,000	58,000	90	46,000	800
Ba	140,000	12,200	71,600	75,000	35,500	30	60,000	600
Co	510,000	144,000	140,000	110,000	$>1\times10^6$	2,200	26,000	550
Cu	400,000	300,000	300,000	11,500	600,000	550	300,000	2,500
Cd	$>1\times10^6$	6,900	170,000	14,500	56,000	340	4,200	120
Pb	155,000	48,600	270,000	92,000	117,000	640	7,400	400
Hg	4,500	670	7,000	2,000	420	300	450	30

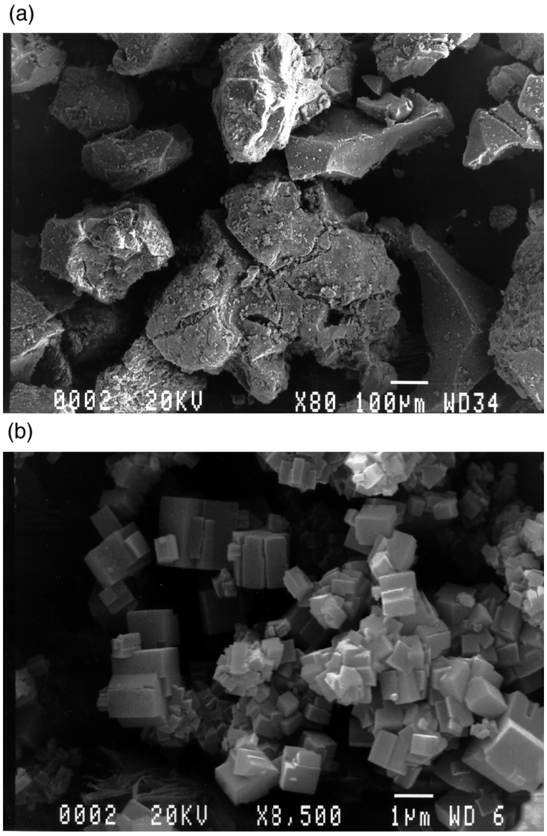

Fig. 2 Scanning electron micrographs showing the morphology of the sodium titanium silicates with 2 days of hydrothermal treatment (a) and 10 days of hydrothermal treatment (b).

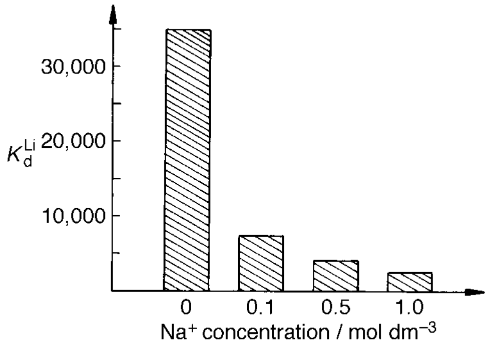

Fig. 3 Li^+ affinity of 7.2 Å phase in the presence of NaCl.

are shown in Fig. 1. The 10.8 Å phase consists of small particles (less than 1 µm), that have irregular form, or their agglomerations. The 7.2 Å phase contains both large particles of irregular form (3–10 µm) and small thin platelets (< 1 µm). The 5.4 Å phase consists mainly of prisms with a square base. Their size varies considerably and some crystals are longer than 10–20 µm. The 5.4 Å phase also contains a significant amount of some amorphous admixture. The type of metastable phase formed depends on the molar ratio of titanium to silicon in the precursor and on the alkalinity of the reaction system. The latter factor is the most crucial because it controls the rate and extent of precursor dissolution and determines the crystallization of the most thermodynamically stable phase under the given conditions. The main trend observed is the formation of titanium silicates with lower Si : Ti molar ratio with an increase in alkalinity of the reaction mixture. Use of concentrated alkali metal hydroxide solutions (2–3 M) results also in a drastic decrease of the mechanical strength of the granules after their hydrothermal treatment from 170–190 to 35–50 kg cm^{-2}, which could be related to the release of the amorphous silicon-containing binder into the solution. An analogous detrimental effect on the mechanical properties of the titanium silicates results from increased time of hydrothermal treatment. The main reason for this is the better crystallization of the compounds. This is evident from examination of SEM images of the $Na_2Ti_2O_3SiO_4{\cdot}2H_2O$ prepared hydrothermally in 2 and 10 days [Fig. 2(a) and (b)]. In the first case the sodium titanium silicate particles are large (up to 500 µm) and have an irregular form, whereas in the second case they are smaller (< 0.5–1.0 µm) and have a well defined morphology, characteristic of this compound. At the same time, preliminary thermal treatment of the precursor at 600 °C considerably favors the improvement of the mechanical strength of the materials obtained (80–100 kg cm^{-2}). However, it changes the type of compounds formed. In particular, two novel metastable sodium titanium silicates were prepared using thermally treated xerogels in mild alkaline media.

The affinity of the granular titanium silicates for alkali, alkali earth and some heavy metal ions was studied in 0.001 M solutions (Table 4). The data shows that the 7.9 and 7.8 Å phases exhibit the highest affinity for Cs^+ ion, whereas the new 7.2 Å phase has the highest affinity for Li^+ ion among the alkali metals. Considering that selective exchangers for Li^+ ion are in great demand, an additional testing of the 7.2 Å phase for lithium uptake in the presence of sodium chloride was carried out. It was found that an increase in NaCl concentration leads to a decrease in the exchanger efficiency to remove Li^+ ion (Fig. 3). This indicates the ion exchange mechanism of Li^+ ion uptake and the existence of Na^+–Li^+ competition for the selective ion exchange sites. Nevertheless, the K_d^{Li} of 2,600 mL g^{-1} in a 1 M NaCl solution suggests that this exchanger is selective for lithium and is promising for some specific separation. Several framework titanium silicates [$Na_2Ti_2O_3SiO_4 \cdot 2H_2O$; ETS4; $Na_2TiSi_2O_7 \cdot 2H_2O$; the 7.2 and 10.8 Å phases, and $K_3H(TiO)_4(SiO_4)_3 \cdot 8H_2O$] exhibit high affinity for heavy alkaline earth metal ions. These ion exchangers show even higher affinity for some other divalent cations, with the only exception being Hg^{2+} ion. In our opinion such extremely high K_d values could be the result of a combined precipitation–ion exchange mechanism of the divalent metal sorption. This mechanism is usually realized for inorganic ion exchangers in metal forms (Na^+, K^+, *etc.*) that easily undergo hydrolysis in aqueous solution, which results in a drastic increase of the pH in the pores of the exchanger (pH 8–9). $Na_2TiOSiO_4$ does not show ion exchange properties, so this compound is not listed in Table 4.

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