Phase distribution in titania–sepiolite catalyst supports prepared by different methods

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In this study it has been shown that in samples prepared by mechanical mixing of titania and sepiolite, greater titania coverages could be obtained when the mixtures were kneaded in a concentrated acid medium. The distribution of sepiolite and titania at the surface of the mechanical mixtures was studied by the electrophoretic migration technique. The samples were further characterised by nitrogen adsorption, XRD and thermogravimetric techniques. The electrophoretic migration results showed that the addition of sepiolite to titania, kneaded in water, had a dramatic effect on the quantity of titanium oxide present at the support's surface, both strongly decreasing the molar fraction of titania at the surface, and altering the electrophoretic properties of the mixtures. When kneaded in concentrated acid (HCl, 37%, m/m), the effect of sepiolite addition was greatly reduced. The XRD patterns and BET surface areas of the water-kneaded samples agreed with previously reported results. However, kneading in acid medium induced a slight increase in the BET surface areas of sepiolite and mixtures, but a small decrease for titania. This acid treatment did not alter the XRD patterns of titania and mixtures, compared to the water-kneaded samples. Although the XRD pattern of sepiolite was partially altered, a large part (71%) of sepiolite remained unchanged.

In commercial processes such as the catalytic oxidation of *o*-xylene to phthalic anhydride,[1] the production of hydrocarbons from carbon monoxide and hydrogen (Fischer–Tropsch synthesis)[2] or the selective catalytic reduction (SCR) of nitrogen oxides,[3] titanium dioxide is widely used as a support. It is also used in processes still under development such as the photocatalytic destruction of volative organic compounds[4] or the splitting of water to give hydrogen, which is used as a fuel.[5]

The combination of titania with a binder has opened the possibility of preparing titania-based monoliths with high mechanical strengths and abrasion resistances.[6] The α-sepiolite [$Si_{12}Mg_8O_{30}(OH)_4(H_2O)_4 \cdot 8H_2O$][7] used as a binder in this study, is a natural fibrous mineral whose fibres range from 0.2 to 2 μm in length and 0.1–0.3 μm[8] in diameter for the bundles of fibres. Its incorporation not only enhances the handling characteristics of the paste to be extruded, but also improves the mechanical properties of the finished monolith which are of great importance for its adoption in industrial applications.[9]

In order to control the parameters affecting the design of the catalyst in this binary support, the distribution of both materials at the surface exposed to the heterogeneous reaction should be studied.

Electrophoretic migration is a useful technique for selectively studying the surface-phase distribution of mixed component solids. This has been previously shown in studies to determine the active phase coverage of supported catalysts.[10–18] The isoelectric point (i.e.p.) of the component materials and the zero point charge (z.p.c.) of their mixtures can be determined.[19] Solid particles are suspended in an electrolyte solution and the zeta potential (ξ) is a function of the solution pH measured. According to our experience the z.p.c. of a mixture is characteristic and lies between the values of the i.e.p.s of the individual components. Thus, the determination of the z.p.c. of a simple mixture of oxides permits calculation of the surface molar fraction of the phases because the z.p.c. is a function of the composition of the exposed surface layer.[10]

The aim of this work has been to study the effects of bulk compositions and kneading pH on the distribution of sepiolite and titania at the surface of the support, when adding sepiolite to titania to improve its rheological and mechanical properties. The effect on the structure and nature of the materials and samples were also studied.

Experimental

Sample preparation

The titania was supplied by Thann et Mulhouse (Courbevoie Cedex, France), with a BET surface area of 81 m^2 g^{-1} and pore volume of 0.27 cm^3 g^{-1}. The α-sepiolite was supplied by Tolsa, S.A. (Madrid, Spain), with a BET surface area of 277 m^2 g^{-1} and a pore volume of 0.35 cm^3 g^{-1}. The samples were prepared by kneading the powders with pure water or aqueous solutions, drying the resulting paste at room temperature for 24 h and heat treating the solid, as described elsewhere.[20] In the case of mixtures, previous mechanical mixing of the two powders was carried out. The mass% contents of titania and sepiolite in the samples are all nominal bulk contents. All high temperature treatments were performed in air for 4 h.

Characterization techniques

The isoelectric points (i.e.p.) of the individual materials and the zero point charge (z.p.c.) of the mixtures as defined by Parks[19] were determined by measuring the zeta potentials as a function of the solution pH. The zeta potentials were obtained using the Helmholtz–Smoluchowski equation[21] $\bar{V}=\frac{1}{4}\varepsilon\xi/\pi\eta$ by measuring the electrophoretic migration rate in a Zeta–Meter Inc. instrument model 3.0+, provided with an automatic sample transfer unit (peristaltic pump and special electric pinch clamp) to avoid sample sedimentation problems. In this equation $\bar{V}$ is the electrophoretic mobility, ε the permittivity, ξ the zeta-potential, and η the dynamic viscosity. Experiments were carried out using 30 mg of 2 μm powder samples suspended in 200 ml of 10^{-3} M KCl, adjusting the pH value with 0.2 M KOH and HCl solutions. Not more than one type of particle was detected in any sample. Each curve was recorded at least twice to ensure reproducibility.

The surface mole fraction of each component in the mixtures was calculated according to the electrophoretic migration method previously described.[10] It is based on the fact that the zero point charge (z.p.c.) of a mixture's surface falls between the isoelectric points (i.e.p.) of the individual materials (A and B). From this principle eqn. (1) and (2)

$$\text{z.p.c.} = X_{\text{A}}(\text{i.e.p.})_{\text{A}} + X_{\text{B}}(\text{i.e.p.})_{\text{B}} \tag{1}$$

$$X_A + X_B = 1 \tag{2}$$

were developed.[10] This permits the molar fraction of each material exposed at the surface to be determined, relating that value with the total composition of the mixture. No further calculations were carried out to obtain the apparent surface coverage (mass% at the surface), as has been done in previous studies,[10–18] because of the inconvenience of assigning a molecular mass to sepiolite from its structural formula $[Si_{12}Mg_8O_{30}(OH)_4(H_2O)_4{\cdot}8H_2O]$.[7]

The surface areas at 77 K were measured using a Micromeritics 1310 ASAP, and determined by application of the BET equation,[22] taking the area of the nitrogen molecule[23] as 0.162 nm^2. The samples were outgassed overnight at 373 K to a vacuum of $<10^{-4}$ Torr to ensure a dry clean surface, free from any loosely held adsorbed species.

Powder X-ray diffraction (XRD) patterns were recorded on a Phillips PW1710 powder diffractometer in the 5–75° (2θ) region using Cu-Kα radiation: $\lambda = 0.1518$ nm.

The TG–DSC curves were measured on a Netzsch 409 EP Simultaneous Thermal Analysis device. Approximately 20–30 mg of powdered sample were heated in air at a rate of 5 K min^{-1} from ambient to 1473 K, using α-alumina as reference.

Results and Discussion

Electrophoretic migration

Fig. 1 shows the zeta potential *vs.* pH curves of titania, sepiolite and their mixtures kneaded in water, all treated at 773 K for 4 h. The i.e.p.s of titania and sepiolite, and the z.p.c.s of their mixtures are listed in Table 1. These values were calculated by interpolation, when possible, and extrapolation, when the z.p.c. was beyond the accessible pH range. The value of i.e.p. of titania, 6.3, was close to that previously reported in the literature, i.e.p. = 6.75.[16] The slight difference between these values could arise from the different origins of the samples. The i.e.p. of sepiolite had not previously been reported, nevertheless the measured value, 2.2, could be compared with that reported for silica, i.e.p. = 3.0,[24] since sepiolite is a silicate.

The effect of the addition of sepiolite to titania is shown in Fig. 1. The presence of sepiolite provoked a large displacement of the z.p.c. to lower values at low silicate contents. This effect became less pronounced at high silicate contents. The z.p.c. reached a value very close to that of pure sepiolite with only 30 mass% present in the bulk composition. This effect is shown in Fig. 2 (squares), where the z.p.c. is represented as a function of the sepiolite content.

The mole fractions of titania at the surface, calculated by applying eqn. (1) and (2) to the results (see Experimental section) are presented in Table 1, expressed as percentages. Concerning these results, it was surprising that the percentage of titania at the surface was greatly decreased by the addition of small quantities of sepiolite. This strong effect of sepiolite 'masking' the titania at the surface can be clearly seen in Fig. 3 (squares), where the mole fraction of titania at the surface *vs.* the titania content is shown. The bulk titania mass% necessary to reach molar fractions >50% at the surface was more than 85%. In that titania was the compound of interest for catalysis, it was worth finding a preparation method that could increase the quantity of titania present at the surface.

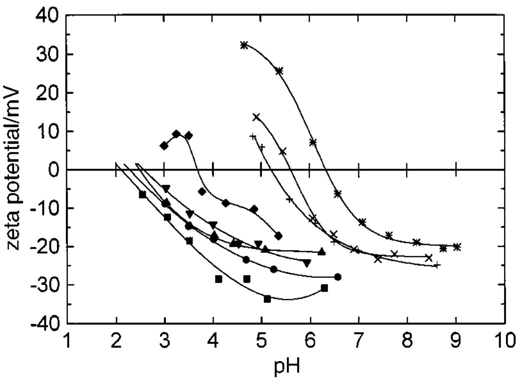

Fig. 1 Zeta potential at 295.7 K as a function of the suspension pH for samples of sepiolite, titania and their mixtures, kneaded in H_2O and treated at 773 K for 4 h. Titania : sepiolite (m/m) (■) 0 : 100 (Tw-1), (●) 30 : 70 (Tw-2), (▲) 50 : 50 (Tw-3), (▼) 70 : 30 (Tw-4), (◆) 85 : 15 (Tw-5), (+) 90 : 10 (Tw-6), (×) 95 : 5 (Tw-7), (✳) 100 : 0 (Tw-8).

Table 1 Properties of TiO_2–sepiolite supports treated at 773 K

sample	composition (% Ti, m/m)	kneading	S_{BET}/ m^2 g^{-1}	z.p.c./ pH	X_{0,TiO_2} (%)
Tw-1	sepiolite	H_2O	149	2.2	0
Tw-2	30		126	2.3	2.4
Tw-3	50		111	2.5	7.3
Tw-4	70		102	2.6	9.8
Tw-5	85		82	3.7	37
Tw-6	90		78	5.2	73
Tw-7	95		72	5.6	83
Tw-8	TiO_2		70	6.3	100
Ta-1	sepiolite	HCl	162	2.2	0
Ta-2	30	(37%, m/m)	122	3.4	32
Ta-3	50		114	4.1	52
Ta-4	70		98	4.7	68
Ta-5	TiO_2		61	5.9	100

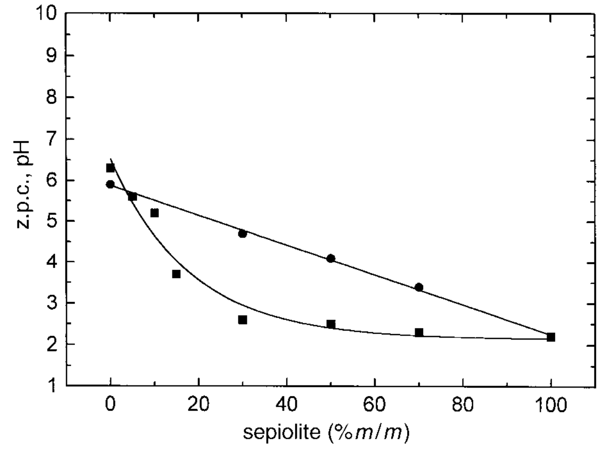

Fig. 2 Variation of the zero point charge (z.p.c.) with sepiolite content of titania–sepiolite mixtures, kneaded in (■) H_2O or (●) HCl (37%, m/m), and subsequently treated at 773 K

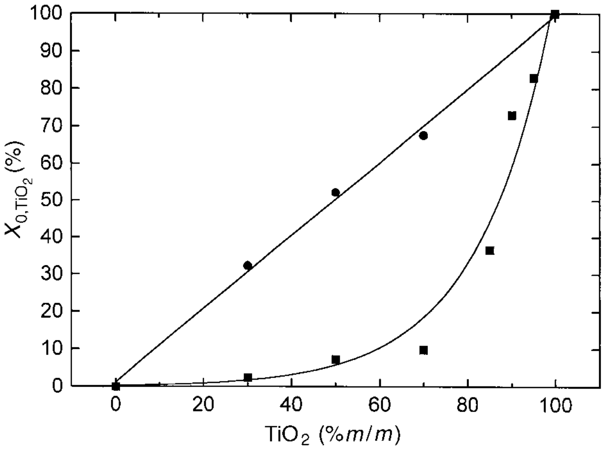

Fig. 3 Variation of the molar fraction of titania at the surface with titania content for titania–sepiolite mixtures, kneaded in (■) H_2O or (●) HCl (37%, m/m), and subsequently treated at 773 K

The mixing behaviour of the two solids could be explained from the thermodynamics and driving forces operating on the interaction of the two components and the morphology of the system during the kneading process. This has been investigated by our group in a previous study[25] for the case of an SCR catalyst based on titania–sepiolite. Sepiolite treated at 773 K was made up of particles with sizes ranging from 100 to 250 µm. These particles were, in turn, composed of bundles of fibres, ranging in size from 0.2 to 1 µm in length and 10–100 nm in width. The titania particles (0.05–0.1 µm) form aggregates of 0.3–1 µm, in which the original particles maintain their identity. According to the model proposed from SEM–EDX, mercury intrusion porosimetry and XRD results, when sepiolite was kneaded with titania and water, the three-dimensional lattice of the sepiolite fibre bundles was destroyed and the particles of titania were dispersed among the fibres.

During the kneading process, the solvent enabled the particles to become mobile, and the system became organised in terms of the driving forces developed in it, which might be affected by the pH. In order to try to alter these conditions and thereby the thermodynamic driving forces of the process during kneading, the pH was lowered by addition of concentrated HCl (37%, m/m). The remainder of the preparation procedure was the same as that used for preparing the other samples.

Fig. 4 presents the zeta potential *vs.* pH curves of the samples prepared by kneading in HCl (37%, m/m). The properties of the resulting samples are summarized in Table 1 (series Ta). The i.e.p. of sepiolite remained the same, although the form of the curve changed, while the i.e.p. of titania was lowered, most possibly due to the protonation of the hydroxy surface groups, that would induce an increase of the surface charge. Considering the z.p.c. values of these mixtures (see Table 1), the effect of adding sepiolite to the titania was much weaker than that of series Tw (Fig. 1). This is shown graphically in Fig. 2 (circles). Comparing series Tw (squares) with Ta (circles) it was observed that the z.p.c.s were much higher, at equivalent sepiolite contents, if the kneading was carried out in an acid medium. A linear regression was used to fit the data, showing that the z.p.c. was linearly related to the sepiolite content.

In order to study the effect of the acid concentration on the z.p.c. of the samples, 50 : 50 (m/m) mixtures were kneaded in a range of acid concentrations. The results presented in Table 2 revealed a linear increase of the z.p.c. with the HCl concentration.

The results obtained with series Ta could be analysed using eqn. (1) and (2) (see Experimental section), calculating the values of titania mole fraction at the surface ($X_{0,\mathrm{TiO_2}}$), expressed in terms of mass% (see Table 1). The results presented in Fig. 3 (circles) followed a linear behaviour. For sample Ta-3 this was a seven-fold increase of the titania at the surface than when kneaded in water. These results could be analysed from another point of view comparing the values of $X_{0,\mathrm{TiO_2}}$ of series Ta with those calculated for series Tw. For example, samples Tw-5 and Ta-2 presented similar molar fractions of titania at the surface (37 and 32%, respectively), while having different titania bulk contents. This example clearly illustrates the effects of acid kneading that could open the possibility of achieving almost the same quantity of titania at the surface using lower amounts of this relatively expensive component.

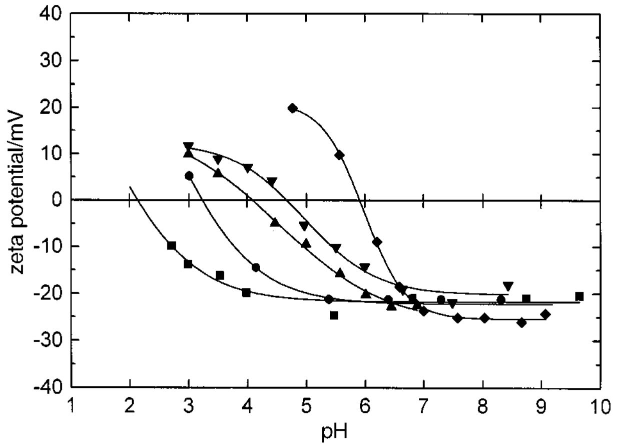

Fig. 4 Zeta potential at 295.7 K as a function of the suspension pH for samples of sepiolite, titania and their mixtures, kneaded in HCl (37%, m/m) and treated at 773 K. Titania : sepiolite (m/m) (■) 0 : 100 (Ta-1), (●) 30 : 70 (Ta-2), (▲) 50 : 50 (Ta-3), (▼) 70 : 30 (Ta-4), (◆) 100 : 0 (Ta-5).

Table 2 Properties of TiO_2–sepiolite (50 : 50, m/m) samples, treated at 773 K and kneaded in HCl

sample	HCl concentration (%, m/m)	z.p.c./pH
Ta-3	37	4.1
Ta-31	20	2.8
Ta-32	10	2.8
Ta-33	5	2.5
Tw-3	0	2.2

To complete the analysis of these electrophoretic migration results, a short comment on the form of the curves should be made. For the Tw series (Fig. 1), the curves that were found to follow the experimental data corresponded to different kinds of sigmoidal and polynomial functions, indicating a clear change in the shape of the curve obtained with titania due to sepiolite addition. This effect was not observed for the Ta series (Fig. 4). The explanation for the changes in the zeta potential *vs.* pH curve shape when mixing two different materials was not clear. To our knowledge, no work has been published to date concerning this point. Nevertheless, this behaviour should be further studied, as it could be related to the mixing process and the surface nature of the materials.

The curves form in Fig. 1 agreed with results reported in 1982,[10] establishing the relation between the coverage by an oxide phase and the z.p.c. determined by electrophoretic migration. However, these new results added another aspect, showing that, not only the z.p.c., but also the form of the curves depended on the coverage, or 'grade of exposure' of the phases at the surface.

Structural characterisation

The structure and surface properties of the samples were studied by nitrogen adsorption isotherms and X-ray diffraction. The results yielded by these measurements were in accordance with previous characterisation results for sepiolite–titania mixtures.[6] The BET surface areas of the Tw materials decreased with increasing titanium content owing to the lower surface area of titania compared to sepiolite. The XRD patterns of the raw materials kneaded in water and treated at 773 K were in accordance with those reported for titania (Tw-8) as anatase (ASTM 21–1272), and anhydrous sepiolite (Tw-1) (ASTM 26–1227). As expected, the rest of the Tw series mixtures patterns were a linear combination of the individual material diffractograms, in accordance with their respective contents with no new peaks detected.

Acid kneading caused a slight decrease, for titania (Ta-5), in the BET surface area (see Table 1). Nevertheless, no change in the XRD pattern (not shown) was detected with respect to sample Tw-8 (titania kneaded in water). A slight increase was observed in the BET surface area of sepiolite, this 'acid activation of sepiolite' effect has been previously reported (HCl,[26] HNO_3[27]).

XRD studies were carried out in order to further study the effect of the acid on the sepiolite structure. The sepiolite that

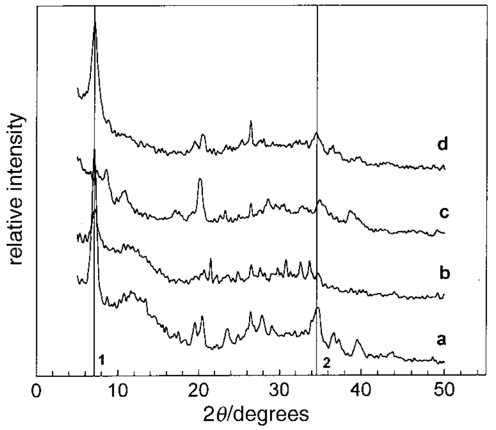

Fig. 5 XRD patterns of sepiolite: (a) kneaded in water and dried at 383 K, (b) kneaded in HCl (37%, m/m) and dried at 383 K, (c) kneaded in water and treated at 773 K, and (d) kneaded in HCl (37%, m/m) and treated at 773 K. Relative intensities calculated with peaks 1 and 2: (a) 100%, (b) 45% and (d) 71%.

was heat treated at 773 K [Fig. 5(c)] was completely transformed to give the characteristic spectrum of dehydrated sepiolite (ASTM 26–1227). The XRD pattern of sepiolite kneaded in acid and treated at 773 K (Ta-1) surprisingly showed the characteristic peaks of the water-kneaded, non-heat-treated sepiolite (ASTM 13–595 and 26–1226), and not those of heat-treated sepiolite (ASTM 26–1227). A quantitative comparison could be carried out with the XRD patterns shown in Fig. 5, all recorded with the same quantity of sample by reference to the two characteristic peaks from untreated sepiolite XRD pattern (ASTM 13–595 and 26–1226) (1, $2\theta=7.1$, $d=12.4$ Å and 2, $2\theta=34.6$, $d=2.6$ Å) [Fig. 5(a)] with those obtained for the samples kneaded in acid, and kneaded in acid and heat-treated shown as curves (b) and (d) in Fig. 5, respectively, because the intensity ratio between both peaks was found to be the same in those samples, indicating that they were only due to the presence of sepiolite. From the calculations, 71% of sepiolite remained unchanged in the sample kneaded in acid and heat treated at 773 K (Ta-1), while this was only 45% in the sample kneaded in acid and dried at 383 K. The remainder was probably amorphous silica, not detected by XRD. Thus, it was surprising that the percentage of unchanged sepiolite increased with thermal treatment. Generally, acid treatments have been reported as 'washings', that is, removing away the solution with the species extracted from the lattice (*e.g.* Mg extraction to obtain silica).[28] When kneading, on the contrary, all the ions remain in the medium. An attempted explanation is that the high-temperature treatment (773 K) could give the system the possibility of being reorganised leading to the recovery of the sepiolite structure.

The BET surface areas of mixtures kneaded in acid decreased with increasing titania content, and their XRD patterns (not shown) were a linear function of the individual materials contents and XRD patterns, with no new peaks, thus indicating that under these conditions no solid-state reactions take place.

In order to complete these results for understanding the effect of acid kneading on the sepiolite structure observed by XRD, the TG–DSC curves of sepiolite kneaded in water (Tw-1) and in HCl (37%, m/m) (Ta-1) were recorded, and are shown in Fig. 6.

Three steps of dehydration of natural sepiolite were reported previously:[29] loss of one molecule of zeolitic water below 470 K; loss of 2.5 molecules in the region 520–620 K; and loss of 0.5 molecules in the region 620–920 K. According to this, the crystal-chemical state of the water molecules has been grouped into three types: zeolitic water, bound water and hydroxy water.[30,31] The curve shown in Fig. 6(a) is in accordance with this, showing two endothermic peaks in the DSC curve but three steps in the TG curve due to loss of water.

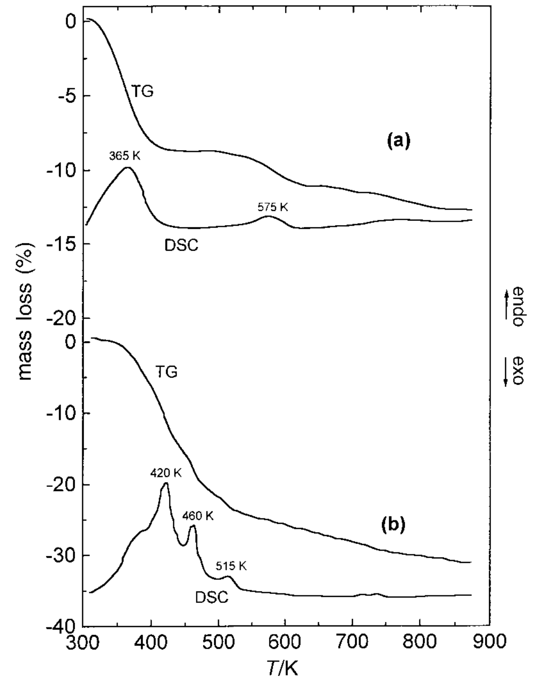

Fig. 6 TG–DSC curves of sepiolite kneaded (a) in water (Tw-1) and (b) in HCl (37%, m/m) (Ta-1)

This was not the case with the acid-kneaded sepiolite. As can be seen in Fig. 6(b), the DSC curve showed a shoulder that could be due to overlapping with the zeolitic water loss and three endothermic peaks in the DSC curve at 420, 460 and 515 K. From the XRD results it was known that there was still 71% of hydrated sepiolite at 773 K, therefore the loss between 373 and 773 K should not be principally due to the loss of bound water. In order to explain this, it has to be taken into account that the HCl content, as the sepiolite was kneaded with 37% HCl, would be lost. The quantity of HCl solution added was that necessary for kneading the sample, *ca.* 50% m/m. This HCl should be present in the air-dried sample, being most possibly lost at low temperatures, and responsible for the three endothermic peaks that were not present in the DSC curve of the sample kneaded in the absence of HCl. This, added water loss (*ca.* 10%), could account for the 27% mass loss that was measured in the range 293–773 K.

Thus, the XRD and thermogravimetric results showed that acid kneading induced a strong change in the behaviour of sepiolite when heat treated, increasing its structural stability to water loss. Nevertheless, these results do not explain why this occurred.

Conclusions

The electrophoretic migration technique was found to be useful for studying the phase distribution at the surface of titania–sepiolite mixtures. The results obtained indicated that the presence of titania at the surface followed an exponential decrease when the sepiolite content of the mixtures kneaded in water was increased. However, the phase distribution at the surface was strongly dependent on the pH of kneading, and kneading in hydrochloric acid increased the quantity of titania present at the surface. Thus, acid kneading leads to the possibility of reducing the titania content needed to obtain a certain quantity of titania at the surface. The titania structure was not altered by the acid presence although a decrease in the BET area was detected. In the case of sepiolite, a slight increase in the BET surface area was produced by acid treatment. Furthermore, from the XRD results the stability of the sepiolite with heat treatment up to 723 K was increased after kneading in acid medium.

We are grateful for the financial aid from the CICYT (Spain), Project AMB93–0244, the CAM (Spain), Project 0057/94, the EC, Project EV5V-CT94–0558 and the FONDECYT (Chile), Project 92–704. We thank Dr. S. Mendioroz for valuable discussions, and Dr. M. Yates for improving the English.

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Paper 7/02077E*; Received* 25*th March*, 1997