Preparation of mesoporous TiO$_2$ by the sol-gel method assisted by surfactants

R. LINACERO, J. AGUADO-SERRANO, M. L. ROJAS-CERVANTES*
Departamento de Química Inorgánica y Química Técnica, Facultad de Ciencias, UNED, Paseo Senda del Rey n° 9, Madrid 28.040, Spain
E-mail: mrojas@ccia.uned.es

Mesoporous titania was obtained by gelation of tetraisopropyl orthotitanate in aqueous or alcoholic solutions with addition of a cationic or anionic surfactant. The gels were dried and calcined to obtain the oxides. The dried samples and the oxides were characterized by thermal analysis, N$_2$- adsorption measurements, infrared spectroscopy, X-ray diffraction and titration with n-butylamine. The effect of the type of surfactant, the chain length of the surfactant and the synthesis method on the textural and surface characteristics of the oxides obtained has been investigated. Cationic surfactants such as dodecyltrimethylammoniumbromide and cetyltrimethylammoniumbromide are effective in controlling the pore size and in increasing the pore volume and the surface area. On the contrary, the sodium dodecylsulphate employed as an anionic surfactant is not incorporated to the hydrous titanium oxide network. The use of a surfactant in the preparation enhances the acid strength of the surface sites of the titanium oxide formed. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

The sol-gel process is a chemical synthesis method extensively applied to the preparation of numerous materials with different chemical properties (glasses, ceramics, adsorbents, catalyst supports). This method allows a control of the texture, composition, homogeneity, and structural properties of the resulting materials [1]. One of the most interesting applications of the sol-gel method is in the field of catalysis. Thus, this method has been successfully used in the preparation of inorganic catalyst supports and supported catalysts [2–7].

Titanium oxide is of particular interest because of its photocatalytic activity [8–10] and use in catalytic oxidation. However, this oxide usually shows a low surface area. Since researchers at Mobil discovered the ordered mesoporous silica MCM-41 [11], there has been great interest in extending the use of surfactant molecules as a template to the preparation of mesostructured materials of other metal oxides [12–17]. Thus, mesoporous titania has been synthesised by using alkyl phosphate surfactants [18], octadecylamine [12, 19], and block copolymers [20], as well as by employing a modified method with cetyltrimethylammoniumbromide as a structure-directing agent [21, 22]. More recently, the preparation of mesoporous titania by templating with polymer and surfactant has been reported [23].

The aim of this work is the preparation of mesoporous and crystalline titania by the sol-gel method through surfactant templating. In this study, two different kinds of surfactant (cationic and anionic) as template were used in the preparation of titanium oxide. These templates were used by mixing them in the alkoxide solution in order to modify the microstructure of the gels and increase the porosity of the resultant titanium oxide. In order to study the effect of chain length, two cationic surfactants have been chosen: dodecyltrimethylammoniumbromide and cetyltrimethylammoniumbromide. These surfactants have been already used in the preparation of other mesoporous materials, such as ZrO$_2$ [24, 25] or silicates [26]. As an anionic surfactant, the sodium dodecylsulphate has been chosen because to our knowledge, there is no literature about the use of an anionic surfactant of sulphate type in the preparation of TiO$_2$. In addition, two different synthesis methods have been used when a cationic surfactant is employed. Therefore, the effects of the ionic nature of surfactant, the chain length of the surfactant and the synthesis method on the textural and surface characteristics of the TiO$_2$ have been investigated.

2. Experimental

2.1. Synthesis procedure

2.1.1. Method 1

This method is similar to that described by Hudson and Knowles [24] and it was applied for the samples synthesised using a cationic surfactant. The gels were prepared by hydrolysis of tetraisopropyl orthotitanate (Fluka) in a Teflon vessel. A 0.1 M aqueous solution of surfactant was alkalinised with NH_4OH (until pH = 11) and added dropwise to the tetraisopropyl orthotitanate in a Teflon vessel under constant stirring at room temperature. The mixture was stirred for 60 min and then heated for 24 h in a bath thermostatically maintained at 80°C. After this time, the mixture was allowed to cool; the solid was separated by centrifugation and washed with water/acetone repeatedly. The surfactants used were dodecyltrimethylammoniumbromide (DTAB, $C_{12}H_{25}N(CH_3)_3Br$) and cetyltrimethylammoniumbromide (CTAB, $C_{16}H_{33}N(CH_3)_3Br$), both solids from Fluka. The surfactant to metal molar ratio (S/Ti) used was 0.5. For comparison, the tetraisopropyl orthotitanate was hydrolysed under identical conditions in the presence of water at pH = 11 without adding surfactant.

2.1.2. Method 2

The synthesis was carried out according to the method described by Pacheco *et al.* [25] for the preparation of zirconium oxide using anionic surfactants. In the present work this method was slightly modified and applied for the samples synthesised using both types (cationic and anionic) of surfactant. When an anionic surfactant is used, a solution containing the surfactant, water and isopropanol was previously acidified with H_2SO_4 acid (until pH = 2) and added dropwise to the tetraisopropyl orthotitanate in a Teflon vessel under constant stirring at 0°C. The sol was aged and stirred for 12 h a 40°C and then it was heated for 24 h in a bath thermostatically maintained at 80°C. After this time, the mixture was allowed to cool; the solid was separated by centrifugation and washed with water/acetone repeatedly. The surfactant to metal molar ratio used was 0.16, and the amount of isopropanol was 30 v/v% in water. The surfactant used was sodium dodecylsulphate (DSS, $CH_3(CH_2)_{11}OSO_3Na$, liquid from Fluka, from which a 0.117 M solution was prepared). For comparison, the tetraisopropyl orthotitanate was hydrolysed under identical conditions in the presence of water at pH = 2 without adding surfactant. When a cationic surfactant is used, the method is similar to that described above, but the surfactant solution was alkalinised with NH_4OH (until pH = 11). Thus, besides the synthesis temperature, the main difference between the method 1 and the method 2 for the preparation of titanium oxide by using a cationic surfactant as template is the presence of isopropanol in the latter case.

The solids prepared by both methods were dried for 24 h at 80°C and calcined for 5 h at 550°C. Data for preparation and nomenclature of the samples are listed

TABLE I Samples prepared in this work

Sample	Method	Surfactant	pH of the preparation
$C_{12}C1$	1	DTAB	11
$C_{12}C2$	2	DTAB	11
$C_{16}C1$	1	CTAB	11
$C_{16}C2$	2	CTAB	11
$C_{12}A2$	2	DSS	2
Ti Isop11	1	–	11
Ti Isop2	2	–	2

in Table I. The samples are designed according to the chain length of the surfactant used (C_{12} or C_{16}), the type of surfactant (cationic, C, or anionic, A), and the method used (1 or 2). Samples prepared without surfactant are named as Ti Isop followed by the value of the pH of the preparation.

2.2. Characterization techniques

The physical characterization was performed on the solids dried at 80°C or calcined at 550°C.

Thermal analysis (TG-DTA) of dried samples was carried out using a Seiko SSC 5200 TG-DTA 320 System. Samples of about 20 mg were heated in air from 30 up to 900°C (flow rate = 75 mL min^{-1}) with a heating rate of 10°C min^{-1}.

The textural characterisation of all samples was accomplished by gas adsorption. The adsorption-desorption isotherms for N_2 at –196°C were measured with the aid of Micromeritics ASAP 2010 equipment. From the N_2 adsorption isotherms, the specific surface area (S_{BET}) was calculated. The pore volume and pore size distribution were estimated by the Barret-Joyner-Halenda (BJH) method [27] applied to the desorption isotherm.

Infrared spectra of dried and calcined samples were recorded in a BOMEM DA3 spectrometer in the 4000–400 cm^{-1} range using the KBr pellet technique.

Crystalline phases of the calcined gels were identified by X-ray diffraction (XRD) using a Seifert C-3000 diffractometer with a nickel filter and Cu-K_α radiation.

Elemental analysis of dried samples was carried out using a Perkin-Elmer CHN 2400 system.

A potentiometric method of titration with n-butylamine was used to determine the total number of surface acid centres and the relative maximum acid strength of the initially titrated surface sites [28] of the calcined samples. A polar solvent such as acetonitrile was chosen in order to avoid the problem of the irreversible adsorption of n-butylamine associated with the use of an inert solvent [29]. Further details of the method can be found in ref. [28]. The electrode potential during the titration was registered on a Titrio DMS 716 digital pHmeter, provided with a combined glass and Ag/AgCl electrode. The experimental method is as follows. A small quantity (0.2 mL) of 0.1 N n-butylamine in acetonitrile was added to 0.15 g of solid and 50 mL of acetonitrile and the system was

kept under steady stirring for 3 h. After that, the titration of the suspension went on using a volume of base solution of 0.1 mL each time. The time elapsed before effecting a potential measurement was 30 s. The maximum acid strength of the first titrated surface acid sites was taken to be the initial electrode potential. The total number of acid sites was estimated from the total amount of base added to reach the plateau in the potential *vs*. volume curve.

3. Results and discussion
3.1. Chemical characterization
The C and H contents of the samples dried at 80°C are listed in Table II. In order to interpret these results, it is assumed that the tetraisopropyl orthotitanate was completely hydrolysed and that the resulting isopropanol, the isopropanol added in some of the cases to the surfactant solution, and the excess surfactant, were washed out by the centrifugation carried out before drying. Hence, the carbon content could be assigned to the remaining surfactant to a first approximation [24]. From these data, the corresponding formulas for the samples were obtained and they are given in Table II. The excess of hydrogen with respect to the hydrogen contained in the surfactant was assigned to adsorbed water. It can be seen that the amount of cationic surfactant incorporated does not depend on the number of carbon atoms of the chain (0.24 for C_{12} and 0.25 for C_{16} by the method 1; 0.11 for C_{12} and 0.13 for C_{16} by the method 2). On the contrary, the synthesis method exerts a marked influence on the amount of surfactant incorporated to the inorganic matrix. Thus, this amount is approximately double for the samples prepared by the method 1 than for the method 2. In any case, only the half of the theoretical surfactant added is incorporated to the hydrous titanium oxide in the most favourable conditions. The method based on the use of DSS as an anionic surfactant is not effective, and the amount of surfactant incorporated is very low (only 0.002 moles of the theoretical 0.16 moles by mol of zirconium).

3.2. Thermal analysis
Fig. 1 shows typical TG-DTA results for $C_{16}C1$ dried at 80°C. Mass loss up to 170°C corresponds to the loss of loosely bond water (5.8 wt%). Although the major removal of water occurs between 30 and 100°C (as observed from the endothermic peak in the DTA curve) there is a steady removal of water up to 170°C, which is consistent with a controlled drying mechanism. Between 170 and 530°C there are three exothermic DTA peaks. These correspond to different stages in the oxidation of the alkyltrimethylammonium species [24]. The last peak (centred at ca. 425°C) probably masks the peak corresponding to the crystallization of anatase, which is detected in the DTA of Ti Isop11, prepared without surfactant. Above 530 °C there are no further mass losses. At this point the residue (51 wt%) is TiO_2. The TG-DTA results for $C_{16}C1$ are typical of the other samples prepared with cationic surfactant, with the amounts of alkyltrimethylammonium incorporated depending on the preparative conditions (method 1 or method 2) and in a less extent of the chain length of the exchanging surfactant (C_{12} or C_{16}).

TABLE II   Results obtained by Elemental Analysis for the samples dried at 80°C

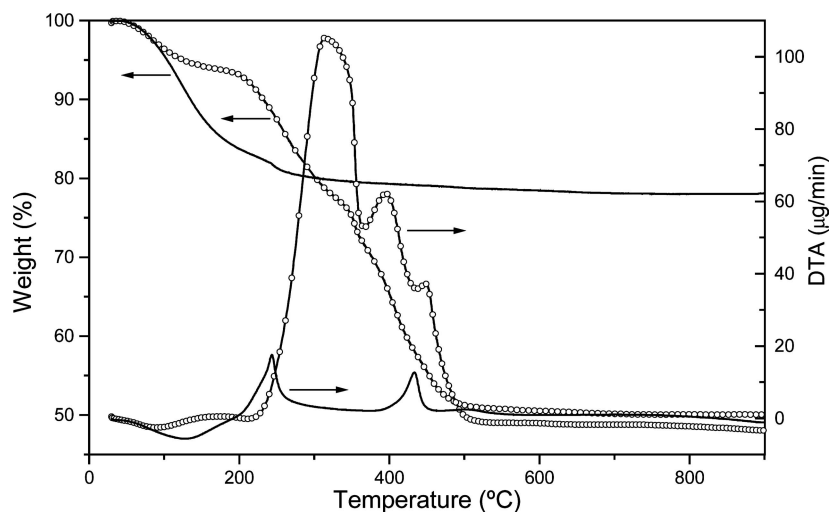| Sample	%C	%H	Theoretical S/Ti ratio	Formula
$C_{12}C1$	24.78	5.07	0.5	$Ti(OH)_4(ODTA)_{0.24}$
$C_{12}C2$	13.88	3.10	0.5	$Ti(OH)_4(ODTA)_{0.11}$
$C_{16}C1$	29.93	6.36	0.5	$Ti(OH)_4(OCTA)_{0.25}$
$C_{16}C2$	18.71	4.28	0.5	$Ti(OH)_4(OCTA)_{0.13}$
$C_{12}A2$	0.28	1.40	0.16	$Ti(OH)_4(ODSS)_{0.002}$

Figure 1 Examples of thermogravimetric and differential thermal analysis obtained with two selected samples. Circle: $C_{16}C1$; straight line: Ti Isop11.

TABLE III Weight losses observed for the samples dried at 80°C

Sample	30–170°C	170–325°C	325–600°C		Total
$C_{12}C1$	6.8	16.2	22.4		45.4
$C_{12}C2$	9.3	8.2	14.8		32.3
$C_{16}C1$	5.8	17	26.2		49.0
$C_{16}C2$	8.4	9.3	19.6		37.3
Ti Isop11	14.1	5.9	1.8		21.8
			325–540°C	540–800°C	
Ti Isop2	11.0	4.5	2.9	5.5	23.9
$C_{12}A2$	12.8	4.6	2.7	7.8	27.9

The curve of hydrous titanium (IV) oxide prepared using aqueous ammonium as the base in the absence of surfactant (Ti Isop11) exhibits a first endothermic peak in the 30–150°C range associated with the loss of water and isopropanol formed in the hydrolysis. This peak overlaps with the exothermic peak starting at 150°C, which could be associated with the decomposition of some remaining OR group of the tetraisopropyl orthotitanate not hydrolysed (the TG curve of the raw tetraisopropyl orthotitanate, not shown for brevity, displays the decomposition of the alkoxide in this temperature range). The exothermic peak centred at 425°C corresponds to the crystallization of anatase because it is not associated with a defined weight loss.

The corresponding weight losses of the different decomposition steps of the samples treated in air are given in Table III. As it can be seen, the weight loss associated with the surfactant loss (between 170 and 600°C) is ca. 1.5 times higher for the samples prepared using a cationic surfactant by the method 1 as compared to those obtained by the method 2. These results indicate the higher incorporation of the surfactant to the hydrous titanium oxide in the first case and they are in agreement with data obtained by chemical analysis. On the other hand, although the amount of surfactant incorporated by a determined method is very similar for the two cationic surfactants used (as seen by chemical analysis), the weight loss observed for the CTAB is slightly higher than for DTAB, probably due to the higher molecular weight of the former (38.6 and 43.2wt% for $C_{12}C1$ and $C_{16}C1$, respectively; 23.0 and 28.9% wt for $C_{12}C2$ and $C_{16}C2$, respectively).

The samples prepared at pH = 2 show a different thermal behaviour to that explained above for the samples prepared at pH = 11, displaying two weight losses in the range 325–800°C (see Table III). The weight loss observed above 540°C is due to the decomposition of the sulphate group proceeding from both the sulphuric acid (for Ti Isop2 and C12A2) and the anionic surfactant (for C12A2) [30], therefore this weight loss being higher for C12A2 than for Ti Isop2. The profile of the sample prepared using an anionic surfactant ($C_{12}A2$) is very similar to that obtained for Ti Isop2 (not shown for brevity). Additionally, the difference in the total weight losses for both samples is very small (only 4wt%) which indicates the low amount of surfactant incorporated to the inorganic

oxide. These results are in agreement with those obtained by chemical analysis.

3.3. FTIR results

Fig. 2 shows the FTIR spectra of $C_{16}C1$ and Ti Isop11 before and after calcinations. All the assignments of the bands present in the spectra have been done according to ref [31]. Regarding the spectrum of $C_{16}C1$ dried, the broad bands observed between 3000 and 3500 cm^{-1} are due to the O–H stretches of water associated with the material. The two sharp bands centred at 2919 and 2850 cm^{-1} are due to the C–H stretches of –CH$_2$ and –CH$_3$ groups of the hydrocarbon chain of the incorporated cetyltrimethylammonium. These bands, which are absent in the spectrum of the Ti Isop11 sample, provide a direct evidence of the incorporation of cetyltrimethylammonium cation into the hydrous oxide. The broad bands at ca. 1600 cm^{-1} are due to the scissors mode of associated water. The sharp bands at ca. 1475–1500 cm^{-1} are due to the C–H deformation of the CH$_2$ and CH$_3$ groups of the incorporated CTAB. The band centred at 1405 cm^{-1} in the spectrum of Ti Isop11 (also present in the spectrum of $C_{16}C1$, although with a very low intensity) can be assigned to the C–H deformation of CH$_2$ groups of residual isopropoxide groups that can remain without hydrolysing. The presence of Ti–O groups, either from the –Ti–O–Ti–O–Ti– polymeric network (for dried samples) or from the Titanium dioxide (for calcined samples) is unequivocally demonstrated by the presence of the strong, but broad band between 500 and 900 cm^{-1}. The spectra of the dried samples prepared with CTAB by the method 2 and DTAB (methods 1 and 2) (not shown for brevity) are very similar to that described for $C_{16}C1$ (method 1), with the presence of the bands assigned to alkylammonium chain, indicating the incorporation of surfactant to the structure. However, in the spectrum of the sample prepared using DSS as an anionic surfactant (not shown for brevity), the intensity of the bands assigned to the surfactant is very low, which indicates the low degree of incorporation of the same to the oxide network, as observed by chemical analysis and thermal analysis. Additionally, some bands between 1030 and 1150 cm^{-1}, which are also observed in the spectrum of Ti Isop2, are present, which can be assigned to H$_2$SO$_4$ used as acid in the preparation.

Looking at the corresponding spectra for calcined samples (see Fig. 2), it can be seen that the calcination at 550°C removed the hydrocarbon chain from the material and the sharp bands at 2900 and 1500 cm^{-1} disappear.

3.4. Textural characteristics

The data of textural characteristics of the samples are given in Table IV. The S_{BET} and V_p values for the dried samples prepared using a cationic surfactant are lower than for Ti Isop11, may be due to the fact that although pores are essentially present in the structure, they are

TABLE IV   Textural characteristics of the samples

	Dried samples			Calcined samples		
Sample	S_{BET} (m^2/g)	V_p^a (cm^3/g)	d_p^b (Å)	S_{BET} (m^2/g)	V_p^a (cm^3/g)	d_p^b (Å)
$C_{12}C1$	9.4	0.094	338.9	50.6	0.195	108.7
$C_{12}C2$	52.4	0.151	125.2	51.1	0.205	116.6
$C_{16}C1$	7.8	0.058	258.9	46.1	0.188	126.7
$C_{16}C2$	18.6	0.132	220.5	36.1	0.156	126.8
$C_{12}A2$	317.9	0.063	50.9	101.6	0.251	62.5
Ti Isop11	375.2	0.194	40.6	25.7	0.129	146.2
Ti Isop2	295.5	0.063	47.6	122.4	0.192	46.8

[a]Vumulative pore volume determined by BJH (desorption branch).
[b]Average pore diameter determined by 4V/A (desorption branch).

blocked by the surfactant. It is necessary to remove the surfactant by calcination to exhibit the mesoporosity. When the samples prepared with cationic surfactant are calcined, the values of V_p and S_{BET} increase significantly, except for $C_{12}C2$, whose S_{BET} values remains unchanged. The sample dried prepared without surfactant (Ti Isop11) shows significant values of S_{BET} and V_p that diminish on calcination. For the calcined samples, the values of S_{BET} and V_p of samples prepared with cationic surfactant are higher (in some cases twice) than for Ti Isop11. As seen by data of chemical analysis, the DTAB was incorporated to the network titanium oxide in a similar degree to the CTAB. However, higher values of S_{BET} and V_p are obtained for the former than for the latter. Thus, curiously a decrease of chain length of the surfactant produces an increment in both values. The synthesis method seems not to exert a clear influence on the textural characteristics of the calcined samples prepared with cationic surfactant. The values of V_p and d_p obtained in the present work are higher than those reported by Yusuf *et al.* [23] in the

preparation of titanium oxide using cetyltrimethylammoniumchloride.

The textural characteristics of dried samples prepared at pH = 2 ($C_{12}A2$ and Ti Isop2) are very similar, which corroborates the low degree of incorporation of the anionic surfactant to the network hydrous oxide, also found by other techniques. When these samples are calcined, the values of V_p increase significantly, especially for the sample prepared with anionic surfactant ($C_{12}A2$), which is the one showing the highest mesopore volume of the series.

The adsorption-desorption isotherms for selected samples calcined are displayed in Fig. 3. The shapes of the isotherms are of type IV, according to the IUPAC classification indicating mesoporosity. The hysteresis loops are, in the case of the samples with surfactant, at higher relative pressures than those corresponding without surfactant, indicating a rather wide range of pore diameter. The hysteresis loop of isotherms of Ti Isop2 is shifted to the left with respect to the rest, indicating the presence of
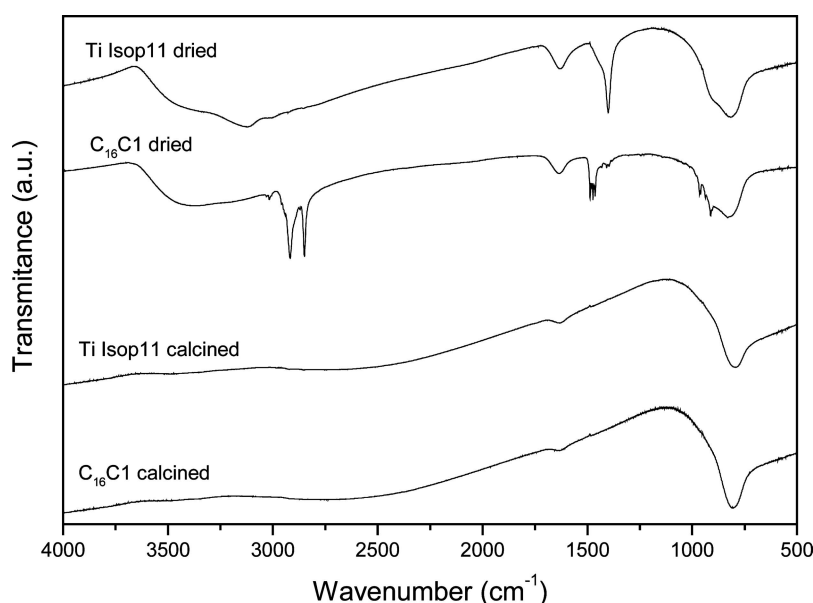

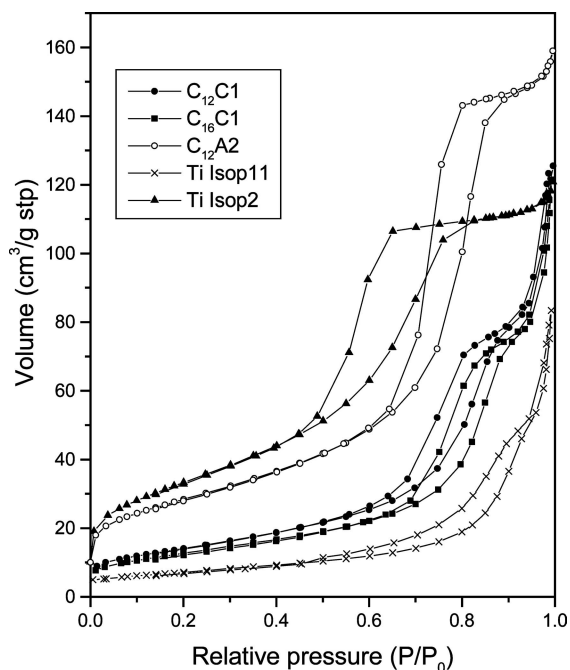*Figure 2* FTIR spectra at room temperature of selected samples.

Figure 3 Adsorption isotherms of nitrogen at –196°C of selected samples.

pores of smaller size in that sample, as can also be seen by its corresponding value of d_p (see Table IV).

Calculated BJH pore size distribution from the desorption branch for some calcined samples are displayed in Fig. 4. The distribution curve of Ti Isop11 shows a bimodal distribution, with two broad peaks centred at ca. 125 and 600 Å. When a cationic surfactant is used in the synthesis the volume of pores of ca. 600 Å increases and a significant amount of pores of size around 80 Å diam-
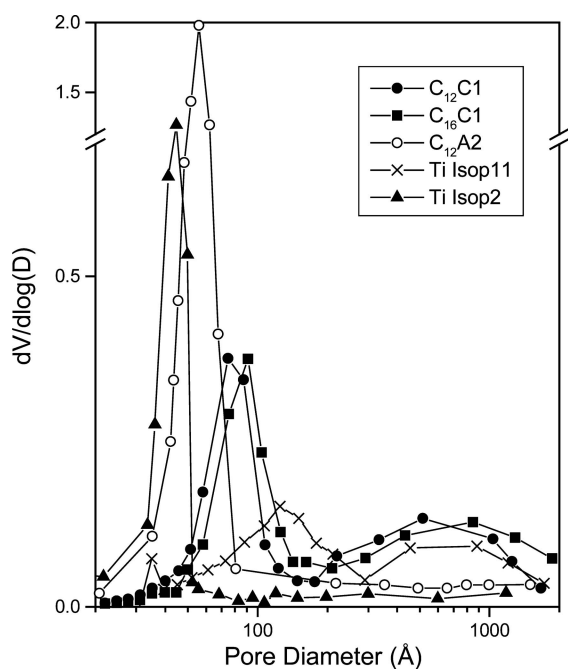

Figure 4 Pore size distributions according to the BJH method calculated from the desorption branches for selected samples.

eter are formed. As seen in the distribution curves, the average pore size of the samples decreases slightly when the length of chain of surfactant decreases (see also the values of d_p in Table IV). At difference of the samples prepared at pH = 11, the samples prepared at pH = 2 (Ti Isop2 and $C_{12}A2$) show a narrow and unimodal distribution, and additionally these samples contain mesopores of smaller size than the rest. As seen above, the $C_{12}A2$ sample is that showing the highest mesopore volume value, but its average pore diameter is lower than for samples prepared with cationic surfactant.

3.5. XRD results
The diffractograms of samples dried at 80°C (not shown for brevity) do not display diffraction peaks throughout the 2θ range between 10 and 80°, which proves that such products are amorphous materials. The corresponding diffraction patterns of the samples calcined at 550°C, which are displayed in Fig. 5, show the presence of anatase. The degree of cristallinity of the anatase phase detected is low, as inferred from the values of average crystallite size listed in Table V, which have been derived from the diffraction peak (101) by applying the Scherrer equation [32]. When a cationic surfactant is used in the synthesis, the average crystallite size of anatase decreases in a factor of 1.2–1.6 with respect to that of the anatase formed in the absence of surfactant (Ti Isop11). The crystal size is slightly affected by the chain length of the surfactant used (lower degree of cristallinity for the samples prepared with DTAB than with CTAB) and in a less extent by the method used in the synthesis. As seen in Fig. 5, the oxides prepared at pH = 2 ($C_{12}A2$ and Ti Isop2) are less crystalline than those synthesised at pH = 11 (the crystal size of Ti Isop11 is double that of Ti Isop2).

3.6. Surface acidity
Here surface acidity was accomplished by a potentiometric method based on the titration with n-butylamine [28]. The titration curves for selected calcined samples are displayed in Fig. 6. The titration curve obtained for the Ti Isop11 is situated below the curves for the series of the corresponding samples prepared using a cationic surfactant. Therefore, the use of such kind of surfactant in the preparation enhances the acid strength of the titrated surface sites. Moreover, the values of the initial electrode potential (E_0) and the potential decrease (ΔV) are set out in Table V. Notice that the E_0 value for the Ti Isop11 is the lowest of all the samples. Since E_0 represents the maximum acid strength of the first titrated surface sites, from the E_0 values it follows that such strength is higher for the oxides prepared using surfactant. Regarding the samples prepared at pH = 2, it can be seen that both samples, Ti Isop2 and $C_{12}A2$ show E_0 values significantly higher than those of the oxides prepared at pH = 11. The Ti Isop2

TABLE V Average crystallite size of the anatase phase and surface acidity of the calcined samples

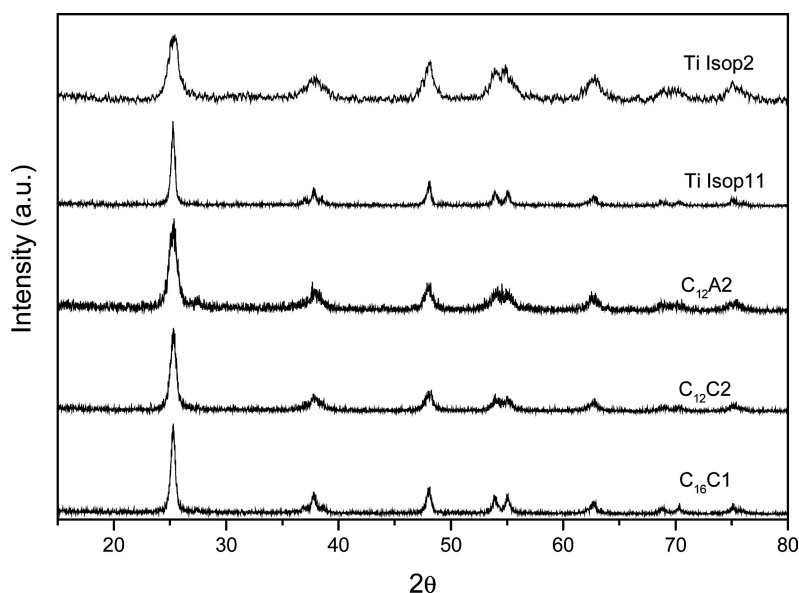| Sample	$C_{12}C1$	$C_{12}C2$	$C_{16}C1$	$C_{16}C2$	$C_{12}A2$	Ti Isop11	Ti Isop2
d (Å)	160	148	185	175	113	222	101
E_0 (mV)	−34	−104.3	−85.2	−107.4	203.9	−156.3	374.5
ΔV (mV)	192.2	118.5	166	132.5	419.7	73.2	584.2

Figure 5 X-ray diffraction patterns for selected calcined samples.
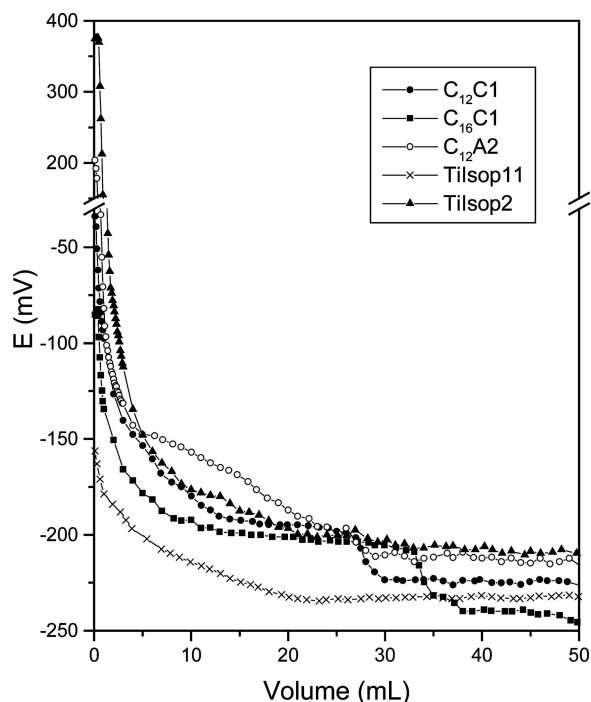

Figure 6 Titration curves with n-butylamine for selected calcined samples.

sample is the one showing the highest acid strength of the series, as it shows the highest E_0 value.

The variation of the potential (ΔV) with increasing volume of base added during titration reflects the differences in the distribution of surface acidity strength of the samples. It can be inferred that the distribution of surface acidity is narrower for the Ti Isop11, as the plateau is reached at ca. 20 mL, and its ΔV value is very low (73.2 mv). The curve for Ti Isop2 also reaches the plateau rapidly (at ca. 25 mL), although the difference of acidity between the initial and the final titrated sites is very high ($\Delta V = 584.2$ mv). On the contrary, the samples prepared using a surfactant (cationic or anionic) have a wider distribution of surface acid sites, as deduced from the two steps clearly distinguished in the corresponding titration curves. This implies the existence in these samples of weaker acid sites, which are titrated by addition of higher volumes of base.

4. Conclusion

Titanium oxides incorporating alkyltrimethylammonium cations of two different chain lengths were prepared by two methods. The amount of cationic surfactant incorporated does not depend on the chain length of the surfactant. On the contrary, the synthesis method exerts a marked influence on the amount incorporated, which is twice higher for the method 1 than for the method 2. The method based on the use of DSS as an anionic surfactant is not effective to incorporate the surfactant to the network of titanium oxide, as deduced by different techniques.

The use of a cationic surfactant increases and in some cases duplicates the S_{BET} values of the titanium oxide

2463

formed. The values of pore volume are also higher for the samples prepared with surfactant.

The increase in the chain length of the cationic surfactant used increases slightly the average pore size of the oxide formed. However, the values of S_{BET} and V_p are higher when a surfactant of shorter chain length is used. The influence of the synthesis method on the textural characteristics is not clear.

The use of a cationic surfactant enhances the acid strength of the surface sites in the titanium oxide formed. The titanium oxides prepared at pH = 2 have stronger acid sites than those prepared at pH = 11. Samples prepared without surfactant show narrower distribution of surface acidity than those synthesised with surfactant, which show the existence of weaker acid sites.

References

1. J. BRINKER and G. SCHERER, Sol-Gel Science. Academic Press, New York, 1989.
2. M. A. CAUQUI and J. M. RODRIGUEZ-IZQUIERDO, *J. Non-Cryst. Solids* **147&148** (1992) 724.
3. R. D. GONZÁLEZ, T. LÓPEZ and R. GÓMEZ, *Catal. Today* (1997) 293.
4. J. B. MILLER and E. I. KO, *Catal. Today* (1997) 269.
5. O. P. KRIVORUCHKO, *Stud. Surf. Sci. Catal.* **118** (1998) 593.
6. M. L. ROJAS-CERVANTES, R. M. MARTÍN-ARANDA, A. J. LÓPEZ-PEINADO and J. DE D. LÓPEZ-GONZÁLEZ, *J. Mater. Sci.* **29** (1994) 3743.
7. M. L. ROJAS-CERVANTES, A. J. LÓPEZ-PEINADO, J. DE D. LÓPEZ-GONZÁLEZ and F. CARRASCO-MARÍN, *ibid.* **31** (1996) 437.
8. F. VICTOR, J. STONE and R. J. DAVIS, *Chem. Mater.* **10** (1998) 1468.
9. N. NEGISHI, K. TAKEUCHI and T. IBUSUKI, *Appl. Surf. Sci.* **121–122** (1997) 417.
10. M. TAKAHASHI, K. MITA and H. TOYUKI, *J. Mater. Sci.* **24** (1989) 243.
11. C. T. KRESGE, M. E. LEONOWICCZ, W. J. ROTH, J. C. VARTULLO and J. S. BECK, *Nature* **359** (1992) 710.
12. D. M. ANTONELLI, *Microp. Mesop. Mater.* **30(2–3)** (1999) 315.
13. U. CIESLA, S. SCHACHT and G. D. STUCKY, *Angew. Chem. Int. Ed. Engl.* **35** (1996) 541.
14. P. LIU, T. LIU and A. SAYARI, *Chem. Commun.* (1997) 557.
15. G. S. ATTARD, *Science* **278** (1997) 838.
16. M. J. MACLACHLAN, N. COOMBS, R. L. BEDARD, S. WHITE, L. K. THOMPSON and G. A. OZIN, *J. Am. Chem. Soc.* **121 (51)** (1999) 12005.
17. J. S. REDDY and A. SAYARI, *Catal. Lett.* **38** (1996) 541.
18. D. M. ANTONELLI and Y. J. YING, *Angew. Chem. Int. Ed. Eng.* **34** (1995) 2014.
19. Y. Q. WANG, S. G. CHEN, X. H. TANG, O. PALCHIK, A. ZABAN, Y. KOLTYPIN and A. GEDANKEN, *J. Mater. Chem.* **11** (2001) 521.
20. N. ULAGAPPAN and C. N. R. RAO, *Chem. Commun.* (1996) 1686.
21. D. KHUSHALANI, G. A. OZIN and A. KUPERMAN, *J. Mater. Chem.* **7** (1999) 1491.
22. D. T. ON, *Langmuir* **15** (1999) 8561.
23. M. M. YUSUF, H. IMAI and H. HIRASHIMA, *J. Sol-Gel Sci. Technol.* **28** (2003) 97.
24. M. J. HUDSON and J. A. KNOWLES, *J. Mater. Chem.* **6(11)** (1996) 89.
25. G. PACHECO, E. ZHAO, A. GARCÍA, A. SKLYAROR and J. J. PRIFIAT, *ibid.* **8(1)** (1998).
26. F. BABONNEAU, L. LEITE and S. FONTLUPT, *ibid.* **9** (1999) 175.
27. E. P. BARRET, L. G. JOYNET and P. P. HALENDA, *J. Am. Chem. Soc.* **73** (1951) 373.
28. R. CID and G. PECCHI, *Appl. Catal.* **14(1–3)** (1985).
29. M. DEEBA and W. K. HALL, *J. Catal.* **60(3)** (1979) 417.
30. H. ARMENDARIZ, B. COQ, D. TICHIT, R. DUTARTRE and F. FIGUERAS, *ibid.* **173** (1998) 345.
31. K. NAKAMOTO, in "Infrared and Raman Spectra of Inorganic and Coordination Compounds", (Wiley: New York, 4thedn)
32. P. SCHERRER, *Nachr. Ges. Wiss. Gottingen* (1918) 96–100.