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Synthesis and Characterization of New Silica-Titania Mixed Oxides Obtained by Sol-Gel Technique

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Summary: Although titanium dioxide has a high surface area, it is not thermally stable and its surface area decreases strongly at high temperature due to phase transformation and crystal growth. To improve the thermal stability of titanium dioxide, the synthesis of mixed oxides can be an elegant approach. In this study different experimental variables for the synthesis and characterization of new titania-silica mixed oxides intended to be used as fillers have been proposed. To manufacture the mixed oxides, different tetraethylortosilicate (TEOS)/Tetrabutyl orthotitanate (TBTi) mixtures in different ratio, ethanol as solvent, and acetic acid as catalyst were used via sol-gel synthesis route. These oxides were characterized by transmission electron microscopy coupled with EDX analysis (TEM-EDX), optical microscopy, X-ray diffraction, textural properties, and pH measurements and wettability with liquids of different polarity.

Keywords: mixed-oxides; sol-gel technique; TEM-EDX; titania-silica; WAXD

Introduction

Titania (TiO_2) has received a great deal of attention due to its use as photocatalyst, white pigment in paints and cosmetics, and filler in adhesives, among others. Although titanium dioxide has a high surface area, it is not thermally stable and its surface area decreases strongly at high temperature due to phase transformation and crystal growth. To improve its thermal stability, the synthesis of mixed oxides can be an elegant route. In this study different experimental variables in the sol-gel technique to obtain new titania-silica mixed oxides intended to be used as fillers were used.

The sol-gel reaction generally occurs in two steps, hydrolysis of metal alkoxides to produce hydroxyl groups in the presence of a stoichiometric amount of water (an acid or base catalyst is generally needed), followed by polycondensation of the resulting hydroxyl groups and residual alkoxyl groups to form a three-dimensional network. Different metal alkoxides based on silicon, aluminum, transition metal alkoxides such as titanium and zirconium have been used as precursors of sol–gel reactions in combination with a variety of organic components.[1] The sequence of reactivity is expressed as follows: $Zr(OR)_4, Al(OR)_3 > Ti(OR)_4 > Sn(OR)_4 >> Si(OR)_4$. However, owing to the loss of volatile by-products formed in the hydrolysis–condensation reactions, it is difficult to control shrinkage during three-dimensional network formation.[2–8]

Factors such as the nature of the alkyl group, the solvent, the temperature, the water-to-alkoxide molar ratio, the presence of acid or base catalysts have been shown to affect the extent of the hydrolysis in the sol-gel reaction.[9] On the other hand, the rate of condensation is slow with respect to the rate of hydrolysis in the presence of an acid

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catalyst, and the resultant material shows a highly ramified low fractal dimensional structure with several silanol groups on the surface.

In this study different experimental variables in the synthesis and characterization of new titania-silica mixed oxides were studied. To synthesize mixed oxides, different tetraethylortosilicate (TEOS)/Tetrabutyl orthotitanate (TBTi) mixtures in different ratio, ethanol as solvent, and acetic acid as catalyst were used in the sol-gel synthesis route. These oxides were characterized by transmission electron microscopy coupled with EDX analysis (TEM-EDX), optical microscopy, X-ray diffraction (DRX), textural properties (S_{BET}), and pH measurements and wettability with liquids of different polarity.

Experimental Part

Synthesis of Silica-titania Mixed Oxides

The main experimental variables used in the sol-gel synthesis of the mixed oxides are shown in Table 1. These oxides were obtained under N_2 atmosphere using tetraethylortosilicate (TEOS) (Aldrich, 99% purity, Argentina) as precursor for silica and tetrabutyl orthotitanate (TBTi) (Aldrich, 99% purity, Argentina) for Titania. Absolute ethanol (Fluka, 99.9% purity, Argentina), distilled water and acetic acid (AcH) (Anedra, 99% purity, Argentina) were used. In all cases, the final products were dried at room temperature.

Experimental Techniques

FTIR Spectroscopy

The oxides were characterized by Fourier transformed infrared spectroscopy using Bruker Tensor 27 equipment (Bruker, New Castle, USA). The IR spectra were obtained in KBr pellets. The pellets were obtained by mixing 0.1 mg oxide in 80 mg KBr (Aldrich, 99 wt% FTIR purity) followed by pressing in a Spectra Tech Qwick Handy Press (Spectra Tech, Connecticut, United States). Two hundred scans were collected at a resolution of 4 cm^{-1} and averaged.

Scanning Electron Microscopy (SEM)

The topographical changes on the oxide surfaces were analyzed using a Jeol JSM840 SEM system (Jeol, Tokyo, Japan). The samples were gold-coated before analysis and the energy of the electron beam was 20 kV. An EDX (Energy dispersive X-ray) analyzer coupled with the SEM instrument

Table 1.
Synthesis parameters of silica-titania oxides obtained via sol-gel.

	Experimental Description					
Oxide	TEOS (ml)	Ethanol (ml)	AcH (ml)	TBTi (ml)	Water (ml)	Observations
Si-1	100	40.5	30			–Stirring during synthesis. After 15 days, the sample began to crystallize.
SiTi-2	100	42.5	30	8.5	32	– The sample was stirred for 24 h. After one week, water was added.
SiTi-3	100	42.5	30	8.5		– The sample was stirred for 24 h. After two days, the gel became yellow.
SiTi-4	100	42.5	30	8.5	16	– The sample was stirred for 24 h. Then, water was added and the gel obtained was white.
SiTi-5	100	42.5	30	8.5	16	– The final wet gel was covered with ethanol in order to obtain fine particles.
Si-6	100	121	30			– More ethanol was added during the synthesis. The final wet gel was covered with ethanol in order to obtain fine particles.
SiTi-7	100	126	30	8.5		– More ethanol was added during the synthesis. The final wet gel was covered with ethanol in order to obtain fine particles.

was used to monitor the chemical composition of the solids. For EDX analysis, the samples were not gold-coated.

Transmission Electron Microscopy (TEM)

A Jeol TEM2010 instrument (Jeol, Tokyo, Japan) was used to analyze the morphology of the oxides; an acceleration voltage of 100 kV was used. The oxides were placed directly into the copper grid especially designed for TEM analysis.

pH Measurements

0.5 g oxide was placed in 50 ml of liquid, and magnetically stirred for 20 min. Several liquids were used: bidistilled and deionized water, absolute ethanol, polyethylene glycol and 1,4-butanediol (all chemical reactants, minimum purity of 99 wt%). The pH values of the solutions were measured at 20 °C in a pH meter with a silver reference electrode in an Instrumentalia SRL digital pH meter.

Textural Properties

The nitrogen adsorption/desorption isotherms at 77 K of the oxides were determined by using Micromeritics ASAP 2020 equipment. The oxides were degassed for 700 min at 100 °C and below 30 μm Hg vacuum. From the isotherms it was possible to determine the specific surface area (S_{BET}), the pore volume, and the mean pore diameter of the oxides.

Results and Discussion

Figure 1 shows the synthesis evolution of sample SiTi-2, taken as typical example, by optical microscopy. In the optical micrographs of SiTi-2 sample, the differences between silica and titania precursors cannot to be established, but a comparison of the micrographs *a-d* to *e-f* shows that in the latter, crystals are seen when their formation begins and when they are already formed. It is important to note that the crystals are formed once water is added to the *sol*. Figure 2 shows the TEM micrograph of SiTi-2, taken as typical example, in which homogeneous particle morphology can be observed.

For comparison, two silicas were obtained: Si-1 and Si-6. The difference between these silica samples is the different ethanol amount added: 40.5 ml for Si-1 and 121 ml for Si-6; TEOS and AcH amounts are the same in both samples. Furthermore Si-1 was synthesized under stirring and, after 15 days, it began to crystallize, but in the synthesis of Si-6, the wet gel was covered with ethanol in order obtain fine particles. The TEM micrographs of Si-1 and Si-6 are shown in Figures 3a and 3b. The silica particles are not finer for Si-6 and the silica morphology is similar in both samples regardless of the different added amount of ethanol. The TEM micrographs shows no difference in the morphology of Si-1 and Si-6, particles are spherical and have a diameter of less than 5 nm.

The textural properties of the different oxides are given in Table 2. All S_{BET} values obtained are very low for a typical mixed oxide (7 m^2/g on average), but close to that of a pure titanium oxide (approximately 10 m^2/g).

Figure 4 shows the nitrogen adsorption-desorption isotherms at 77 K of Si-1 and Si-6. The specific surface areas of the oxides were obtained by applying the BET equation developed by Brunauer, Emmett and Teller to the adsorption isotherms of nitrogen at 77 K in the range of relative pressure between 0.05 and 0.30. The BET equation can be expressed as follows[10]:

$$\frac{P}{V(P_o - P)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C}\,\frac{P}{P_o}$$

where P_o is the saturation vapor pressure, V_m is the monolayer capacity, and $C = \exp[-(\Delta H_{ads} - \Delta H_{liq})/RT]$.

The S_{BET} values of Si-1 and Si-6 samples are 6.1 and 8.0 m^2/g, respectively. These values, as well as the pore volume, are relatively similar for both oxides (Table 2), but their pore diameters are 115.4 and 67.7 Å, respectively. This variation could be attributed to pores formation during drying, and the excess of ethanol could also influence the intra- and extra-particle pore formation.

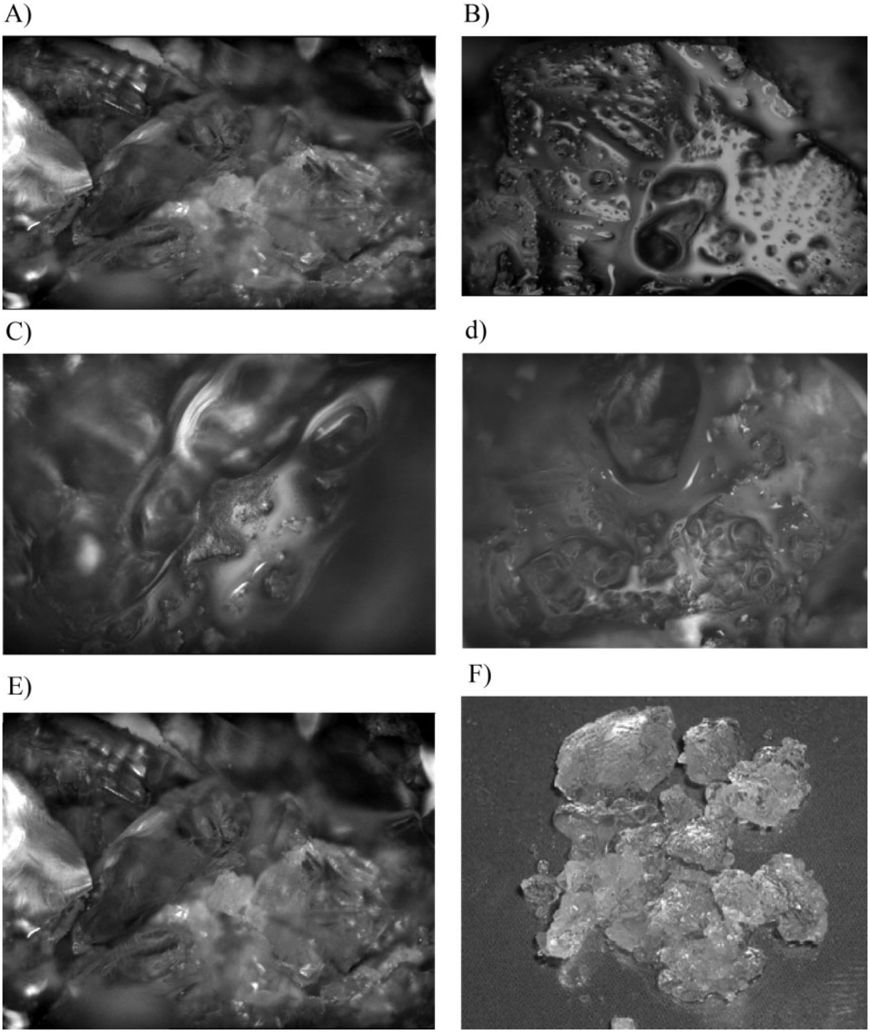

Figure 1.
Optical micrographs of SiTi-2 oxide (500 ×).

The nitrogen adsorption-desorption isotherms at 77 K correspond to the type II in the BDDT classification, into which pure silica samples usually are classified. However, considering their hysteresis loop, i.e., the isotherms do not follow the same path for adsorption/desorption, they can be more precisely classified as type VI. This behavior could be ascribed to the fact that the evaporation of the condensed gas in fine pores is not as easy as in the condensation process. These results are in agreement with those obtained by Zhang *et. al.*[11] in which the silica-titania oxides show low adsorption capacity and almost no hysteresis. Considering that the titania content may lead to the TiO_2 agglomeration during sol–gel process, and this agglomeration will close some mesopores and cause the breakage of the SiO_2 and TiO_2 interface, it can be anticipated a reduction in surface area and a lower pore volume.

The TEM micrograph of SiTi-3 oxide is shown in Figure 5. The gel was stirred for one day and after two days, a yellow colour appears. The amounts and ratio of reactants

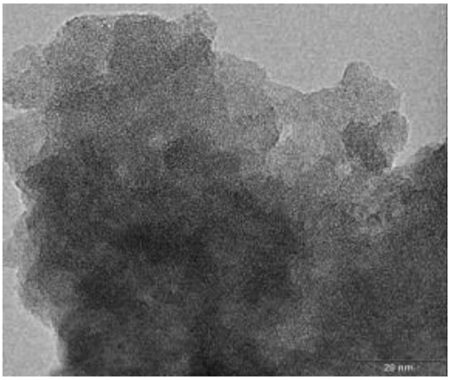

Figure 2.
TEM micrograph of SiTi-2 oxide (scale: 20 nm).

Table 2.
Textural properties of the oxides.

Sample	S_{BET} (m^2/g)	Pore size (Å)	Pore volume (cm^3)
Si-1	6.1	115.4	0.017
SiTi-2	5.9	102.2	0.015
SiTi-3	6.6	84.8	0.014
SiTi-4	7.6	74.8	0.014
SiTi-5	9.0	74.6	0.016
Si-6	8.0	67.7	0.013
SiTi-7	10.1	64.7	0.016

are shown in Table 1. Nucleation occurs in spherical form between both precursors, TEOS and TiBTi. However, the particle size of the silica-titania oxide is smaller and it is not easy to discriminate between silica and titania nuclei. The dry solid is some-

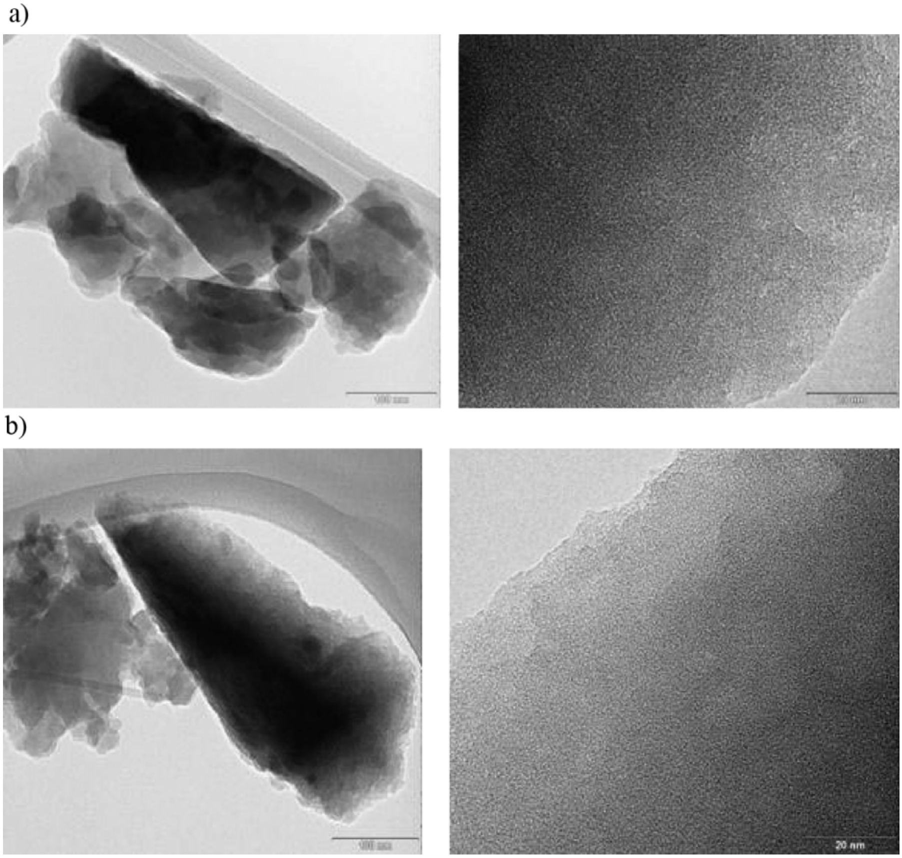

Figure 3.
a) TEM micrograph of Si-1 oxide (scale: 100 – left - and 20 nm - right), b) TEM micrograph of Si-6 oxide (scale: 100 – left - and 20 nm - right).

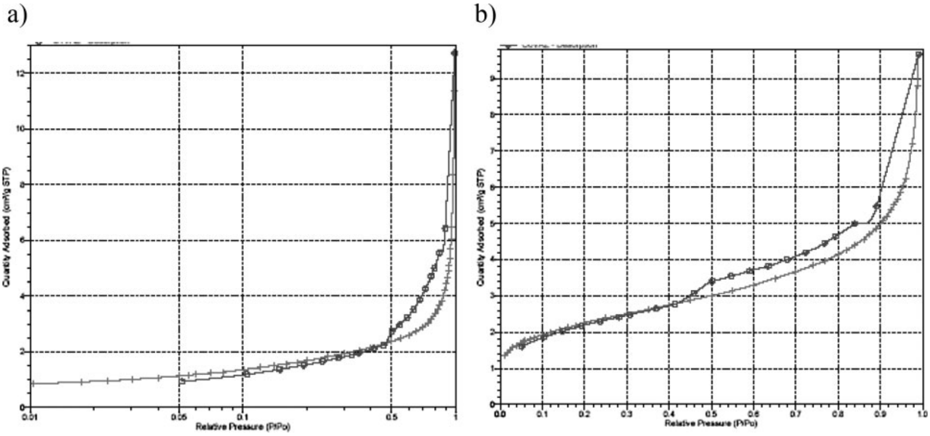

Figure 4.
Nitrogen/77 K adsorption-desorption isotherms of Si-1 (a) and Si-6 (b).

what darker than pure white silica, but the yellow colour of the wet gel disappears. This colouration could be due to particle agglomeration, which is more evident than in the other synthesized oxides. According to the S_{BET} values (Table 2), the SiTi-3 oxide has a surface area of 6.6 m^2/g, which is the same as that of the other mixed oxides. Pore diameter and volume values are also similar.

The TEM micrograph of SiTi-4 oxide is shown in Figure 6. Unlike the SiTi-3 oxide, after stirring for 24 h, water was added. The obtained gel maintained its white color. Despite particle agglomeration (Figure 6), the S_{BET} is 7.6 m^2/g. The nitrogen adsorption isotherm corresponding to this sample is shown in Figure 7. Interestingly, the adsorption and desorption are similar, i.e. there is no hysteresis, although the pore diameter and pore volume values are very similar to those of the other oxides. This could be related to the different texture of this oxide.

TEM micrographs of SiTi-5 and SiTi-7 oxides are shown in Figure 8. According to Table 1, different experimental conditions were used during their synthesis. In both oxides, the wet gel was covered with excess ethanol in order to obtain finer particles. In neither case homogeneous particle morphology was obtained, although the TEM micrograph of SiTi-5 shows the presence of similar spherical particles than in the pure

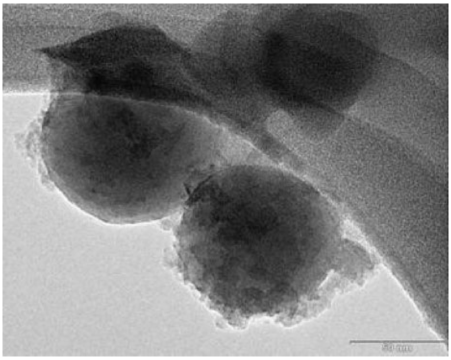

Figure 5.
TEM micrograph of SiTi-3 oxide (scale: 50 nm).

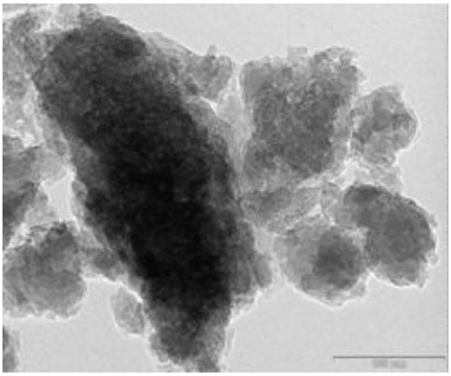

Figure 6.
TEM micrograph of SiTi-4 oxide (scale: 100 nm).

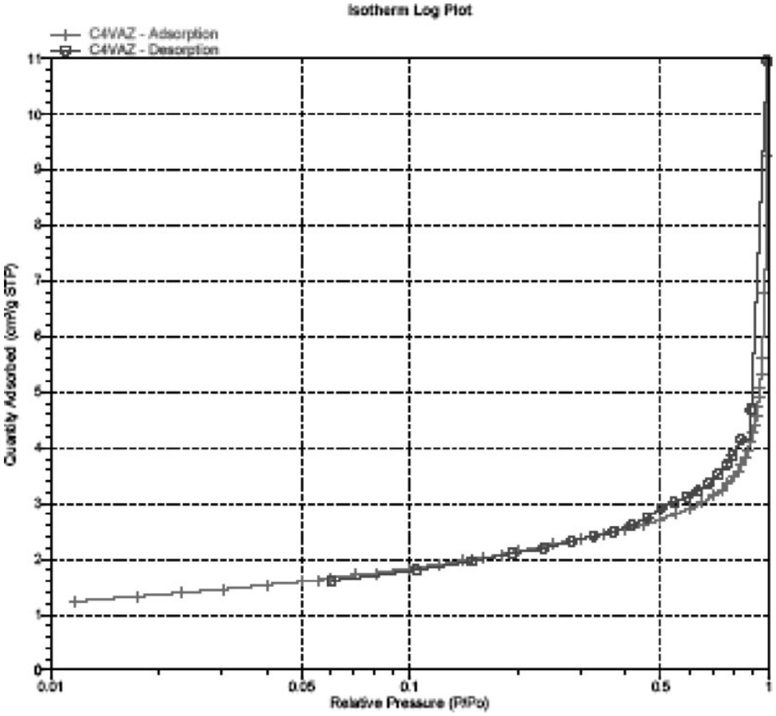

Figure 7.
Nitrogen/77 K adsorption-desorption isotherm of SiTi-4 oxide.

silica. This behavior could be due to nucleation of silica and coating by titania. Anyway, this is not evidenced by EDX. However, Calleja *et.al.*[12] analyzed by EDX different areas of 0.1 μm^2 belonging to different and thin particles and they determined their chemical composition indicating the homogeneity of their xerogels. In our case, therefore, it should necessary to analyze the chemical composition of these oxides by using additional more sensible surface analysis techniques.

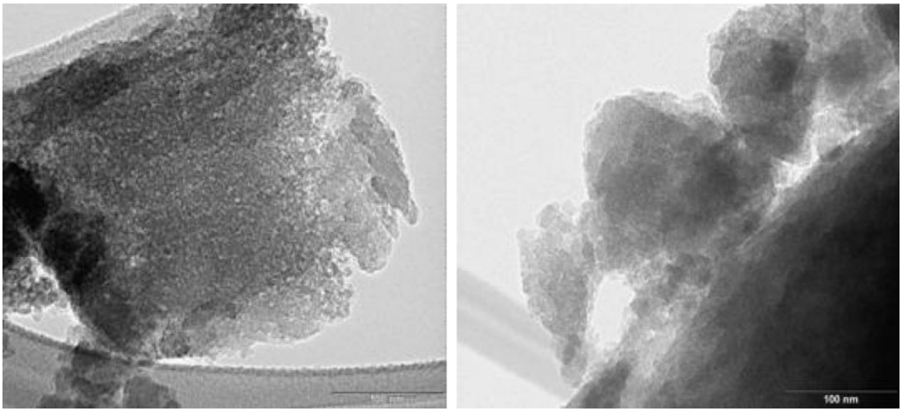

Figure 8.
TEM micrographs of SiTi-5 and SiTi-7 oxides (scale: 100 nm).

On the other hand, the textural analysis of the samples provides a S_{BET} of 9.0 m^2/g for SiTi-5 and 10.1 m^2/g for SiTi-7. Although these values are somewhat similar, their pore diameters are 74.6 and 64.7 Å, respectively.

The X-ray diffractograms of the mixed oxides and pure silica (Si-1 and Si-6) are shown in Figure 9. In all cases the phases of the oxides are noncrystalline and none of them shows evidence of a different phase despite the different experimental variables

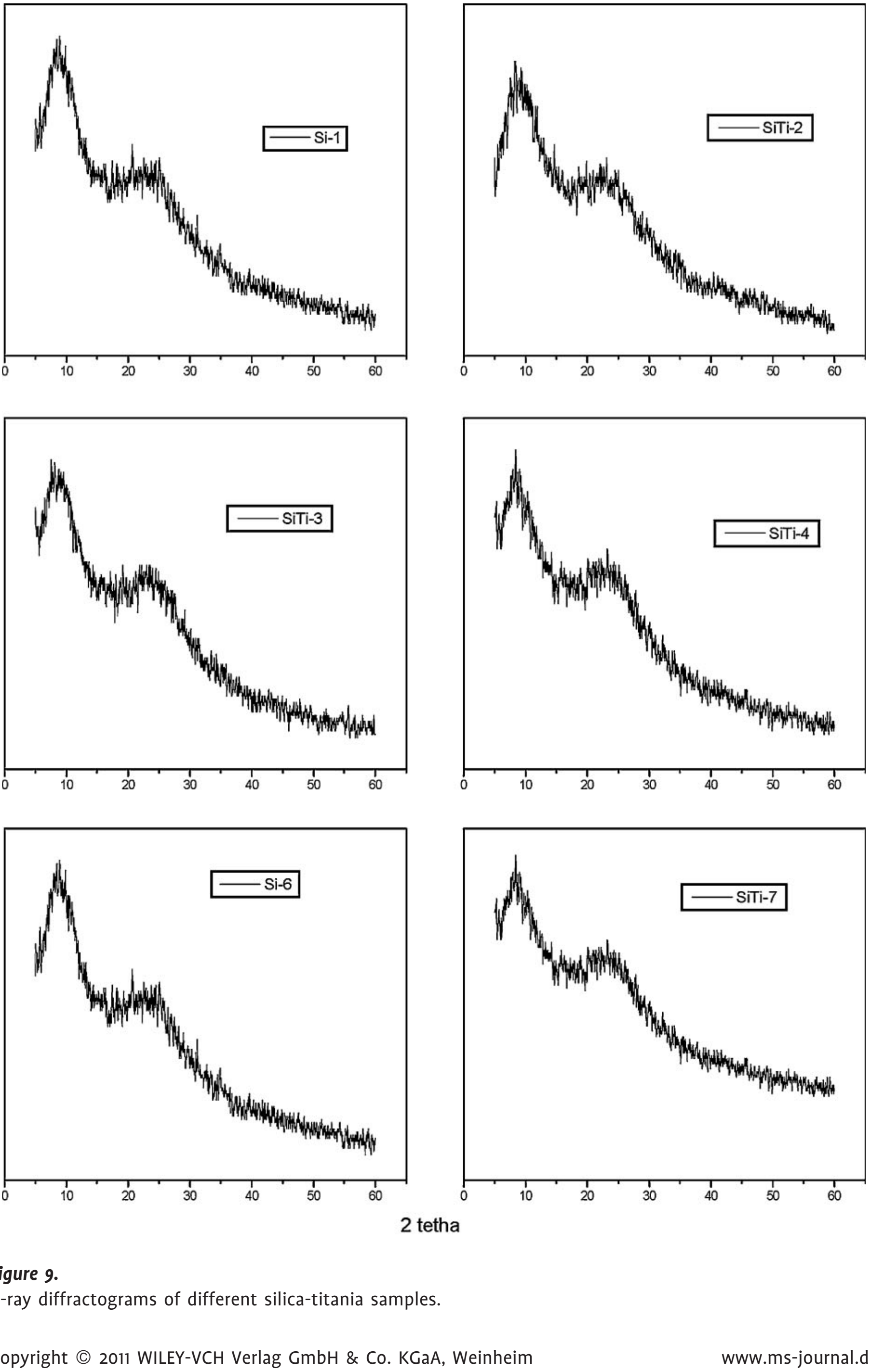

Figure 9.
X-ray diffractograms of different silica-titania samples.

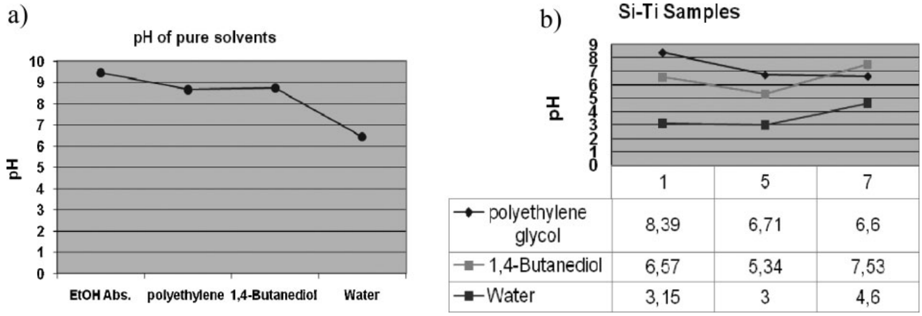

Figure 10.
a). pH of solvents, b). Wettability of Si(Ti)-1/7 sample.

using during their synthesis. Calleja *et.al.*[12] have found that the wide-angle X-ray diffraction analysis of several xerogels revealed an essentially amorphous character in all these materials.

Figure 10a) shows the pH values of the solvents used to measure the wettability of the oxides. Absolute ethanol, polyethylene glycol and 1,4-butanediol have similar pH (9.5-8.5), whereas water has a pH of 6.4. Figure 10b) shows the pH of the oxides (the curve of the absolute ethanol is not shown because of its similarity to that of water). hen water is put in contact with the oxides, the pH decreases due to lixiviation or dissolution of the gel phase. The same decrease in pH are obtained by placing the oxide in contact with polyethylenglycol or 1,4-butanediol (pH between 5.5 and 5). In fact, the polarity of the solvent prevails over the sample morphology since all oxides show similar pore volume (Table 2). To compare this test with other similar realized by Hilonga *et al.*[13] carried out this kind of test by using dioctyl phthalate and they concluded that the wettability of dioctyl phthalate of composites can be related to their surface area or porosity.

Conclusion

In this study new silica-titania mixed oxides were synthesized by polymerization of TEOS and TBTi mixtures by the sol-gel method. Different gels were prepared with one initial SiO_2-TiO_2 content but different ethanol and water amounts. Surface area and porosity of the samples were measured; X-ray diffraction technique was used to determine the crystallographic structure of the inorganic constituent of the mixed oxide. In order to analyze the morphological changes and particle size, the oxides were characterized by SEM and TEM. Although differences in morphology were obtained, they did not correlate with the texture and particle size of the mixed oxides, and additional research efforts will be necessary to obtain more definitive results. Finally, the samples were placed in contact with solvents of different polarity to study the lixiviation or dissolution of the gel phase.

This study has a potential interest in the growing area of the development of nanocomposites from organic polymers and TiO_2 or amorphous SiO_2 nanoparticles. In fact, in the design of nanocomposites with such nanoparticles, hazard reduction extending to the full nanocomposite life cycle would seem a matter to consider. Options for hazard reduction includes the changes of the nanoparticle surface, structure or composition, better fixation of nanoparticles in nanocomposites, including persistent suppression of oxidative damage to polymers by nanoparticles, and design changes leading to the release of relatively large particles.[14]

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