Articles

Mesoporous Silica Modified with Titania: Structure and Thermal Stability

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Mesoporous silica modified with titania was prepared using the sol−gel process. The structure of these composites was studied using infrared and UV−visible spectroscopies, thermogravimetry, nitrogen sorption measurements, and scanning and transmission electronic microscopies. In light of these results, a model of formation was proposed: the material is composed of a mesoporous silica matrix and small titania particles mainly located at the surface of pore walls. The thermal stability of these composites was investigated from 650 to 1000 °C. It was shown that the increase in temperature leads to the growth of titania nanoparticles associated with the shrinkage of the mesoporous structure. Nevertheless, the whole structure remains mesoporous until 850 °C; the thermal stability is thus improved compared to pure silica or pure titania. At 1000 °C, the composites are nonporous and contain crystallized anatase titania nanoparticles with a mean diameter between 5 and 10 nm embedded in the silica matrix.

1. Introduction

Titania (TiO_2) is an important material that is used as a support for catalysts[1] and has excellent photocatalytic properties. These properties, together with its superhydrophilicity, are the base of the wide applicability of titania in liquid-phase pollution control, decomposition of organic contaminants, environmental purification, production of hydrogen gas, fabrication of self-cleaning building materials, and antimicrobial tiles.[2] The photocatalytic activity of titania is governed by various parameters, e.g, particle size, texture/reactive surface area, bulk and surface perturbations, and crystal structure.[2−5] Moreover, the photocatalytic activity can be influenced/improved by incorporation of the titania on/into nonreactive, photoinert support material. Good candidates for supports are mesostructured silicas (MS) of the MCM or SBA type because of their high surface areas, ordered frameworks, and narrow pore size distribution.[6,7] The anatase phase of titania, which is generally more efficient than the rutile phase, can be preserved to higher temperatures in such SiO_2−TiO_2 nanocomposites in comparison with the bulk TiO_2.[2,8,9] The anatase phase is metastable and transforms to the rutile structure at temperatures above 500 °C.[2,3,10] It was shown that titania−silica nanocomposites have the anatase phase even after calcination up to 900 °C.[11] Moreover, the high temperature of the calcination can reduce bulk defects inside the titania particles.[2,3,12,13] The interaction between titania and silica can produce new active sites, which can extend the possibility of the application of the materials.[14]

In this context, the present paper deals with the incorporation of titania nanoparticles into a silica matrix, with the whole system being mesoporous. Samples with different Ti:Si mass ratios were prepared (5, 10, 15, and 30 wt %) and characterized using IR and UV−vis spectroscopy, nitrogen sorption measurements, electronic microscopy (SEM and TEM), and X-ray diffraction. The thermal stability of the

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composite samples and evolution of the titania phase from 650 to 1000 °C was also investigated. In light of the results obtained, a model of formation of the mixed SiO_2-TiO_2 mesoporous matrix was proposed.

2. Experimental Section

2.1. Preparation of the Ti−Si Mesoporous Samples. All chemicals were procured from Aldrich and used as received without further purification. The tetraethoxysilane (TEOS) and titanium isopropoxide (TTIP) were used as silica and titania sources, respectively. Pluronic F127 ($EO_{106}PO_{70}EO_{106}$; where EO = CH_2-CH_2O, PO = $CH_2(CH_3)CHO$; M_{av} = 12 600) was used as a structure-directing agent.

Mixtures consisting of Pluronic F127, butanol, H_2O/HCl, and TEOS/TTIP with the mass ratio 1:0.428:1.58:3.13 were used in the synthesis. In a typical procedure, a mixture of TTIP and TEOS with a varying Ti:Si mass ratio was prepared first (5, 10, 15, and 30 wt % for samples denoted as **MTi5**, **MTi10**, **MTi15**, and **MTi30**, respectively). Butanol was then added to this mixture, and the solution was heated to 60 °C with stirring while evaporation was prevented. In the subsequent step, Pluronic F127 was added and the mixture was stirred for 30 min. Finally, 0.1 M HCl was added dropwise. The solution was stirred at 60 °C for 30 min. The beginning of the gelation was observed after this time; as the temperature decreased, a white gel was formed. The gel was dried at room temperature for one week. White monoliths of as-synthesized samples were recovered. The organic component was removed from the as-synthesized samples by calcination in a flow of synthetic air in two steps. In the first step, the sample was heated at 5 K/min up to 300 °C and kept at this temperature for 3 h. In the second step, the temperature was increased from 300 to 550 °C at 0.5 K/min; the sample was kept at this temperature for 7 h.

To study the thermal stability and phase evolution of titania, we subjected the as-calcined samples to thermal treatment to 650, 850, and 1000 °C. During this treatment, the as-calcined samples were heated in a static air atmosphere at rate of 1 K/min to temperatures of 650, 850, or 1000 °C. The samples were then kept at the respective temperature for 7 h and finally cooled to room temperature at a rate of 2.5 K/min.

2.2. Characterization Methods. The infrared spectra of the complexes were recorded with an EQUINOX 55 (Bruker) FT-IR spectrophotometer as KBr disks (1:100 sample:KBr mass ratio). The diffuse−reflectance UV−vis spectra were recorded with a SPECORD-M40 spectrometer using barium sulfate as the reference material. Thermogravimetric (TG) measurements were carried out under a dynamic nitrogen atmosphere (sample flow rate of 60 mL/min) using hi-res mode (G) and an initial heating rate of 10 °C/min by means of a TGA Q500 apparatus (TA Instruments). Nitrogen adsorption−desorption experiments were carried out with an ASAP 2010 Micromeritics apparatus at 77 K. Prior to adsorption, samples were outgassed under a vacuum for 24 h at 150 °C. SEM micrographs were taken with Cambridge S-90 and Philips XL 30 ESEM instruments. TEM micrographs were taken with a JEOL 2000FX microscope. XRD patterns were measured on a Siemens D5005 XRD diffractometer using Cu Kα radiation.

3. Results and Discussion

3.1. Effect of the Amount of Titania Inserted on the Mesoporous Structure. *Thermogravimetry.* The results of TGA (not shown) of the as-synthesized samples show similar curve shapes. An initial weight loss of 5% below 100 °C was followed by a weight loss of 50% in the range from 200 to 550 °C, corresponding to the pyrolysis of the organic template. An increase in the amount of titania in the samples led to a lower onset of decomposition. This small difference can be related to the catalytic activity of titania.

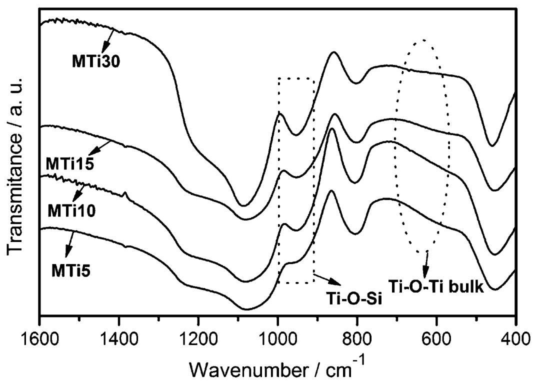

Figure 1. FT-IR spectra of samples **MTi5**, **MTi10**, **MTi15**, and **MTi30**.

Infrared Spectroscopy. The FT-IR spectra of as-calcined Ti−Si samples **MTi5**, **MTi10**, **MTi15**, and **MTi30** are in Figure 1. The bands of Si−O−Si vibrations dominate in the IR spectra. The ones around 1080 cm^{-1} (with a shoulder around 1210 cm^{-1}) and 804 cm^{-1} are due to asymmetric and symmetric Si−O−Si stretching modes, respectively. The band around 457 cm^{-1} is assigned to the Si−O−Si bending mode.[15,16]

Moreover, the bands around 953 cm^{-1} were observed in the spectra of all samples. The bands in this region (910−960 cm^{-1}) are characteristic of the presence of framework titanium and vibrations of Ti−O−Si bonds.[14,17−25] Their positions are sensitive to the chemical composition of the samples, and their intensity depends on the absolute amount of the Ti−O−Si linkages.[14,17−20] From Figure 1, it is obvious that the intensity of the bands increases from sample **MTi5**, containing the lowest amount of titania, to sample **MTi30**, with the largest amount of titania. Moreover, small differences were observed around 620 cm^{-1} in the spectra of samples **MTi5**−**MTi30**. The bands in this region can be assigned to the vibrations in the TiO_2 bulk phase.[23] The evolution of this band was further observed during thermal treatment of the samples to higher temperatures (see section 3.2).

Diffuse−Reflectance UV Spectra. The diffuse reflectance UV spectra of samples **MTi5**, **MTi10**, **MTi15**, and **MTi30** are presented in Figure 2a. The samples show broad bands

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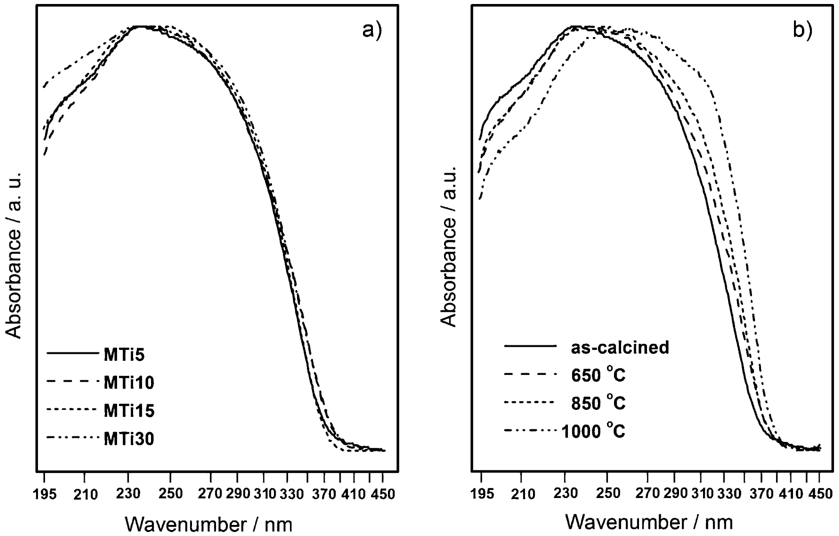

Figure 2. Normalized UV spectra of (a) samples **MTi5**, **MTi10**, **MTi15**, and **MTi30** and (b) sample **MTi5** thermally treated at 500, 650, 850, and 1000 °C.

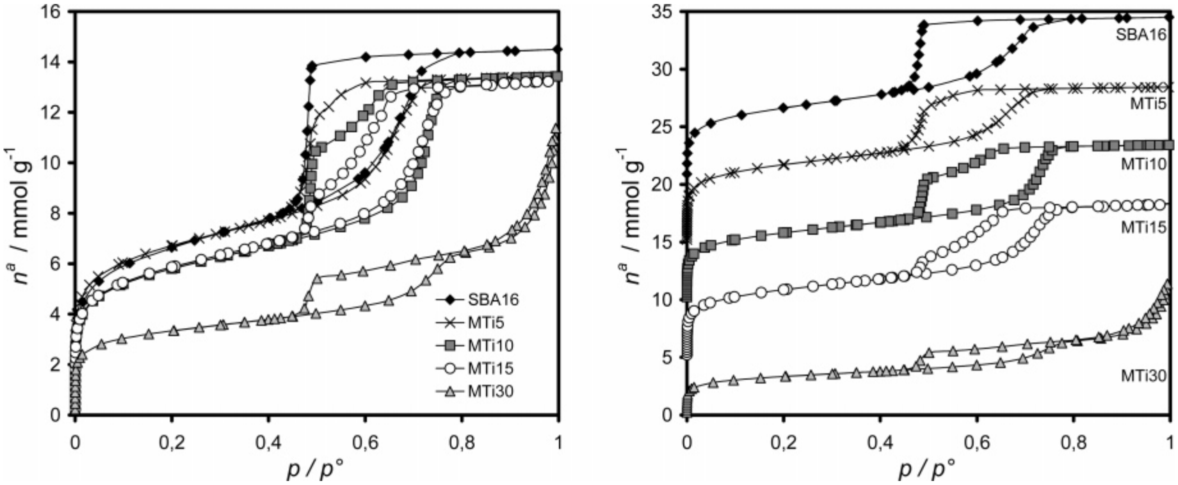

Figure 3. Nitrogen adsorption−desorption isotherms of as-calcined samples **MTi5**, **MTi10**, **MTi15**, and **MTi30**.

in the range 195−400 nm due to adsorption by titanium species. The broad nature of these bands suggests that the bands are formed by the superposition of several signals: Ti species incorporated in the silica framework and individual TiO_2 particles.

First, the slight shoulder around 210 nm was observed in the UV spectra of titania-containing samples. Generally, the adsorption bands around this region are assigned to isolated, tetrahedrally coordinated Ti(IV) framework sites.[26,27] We suppose that these shoulders are due to the incorporation of the titanium ions into the silica framework and the formation of Ti−O−Si linkages. This result is in accordance with the infrared spectra discussed above.

The maximum in the UV spectra of all four samples is observed between 230 and 260 nm. The spectra in this region are sensitive to dispersion and hydration states and can be assigned to Ti species with 5- and 6-fold coordination.[26] The absorbance above 300 nm is indicative of the presence of TiO_2 particles in the porous system of MS or on the pore walls.[28]

Nitrogen Adsorption/Desorption Measurements. The nitrogen adsorption−desorption isotherms are given in Figure 3. The five isotherms in Figure 3a correspond to the pure silica sample as well as the samples prepared with 5, 10, 15, and 30 wt % titania. Figure 3b shows the same isotherms, each offset to allow for a clearer comparison. In general, these isotherms correspond to type I and type IV behavior, indicative of the presence of both micropores and mesopores.[29]

The adsorption at low pressures, below a relative pressure of 0.05, indicates microporosity that probably results from the partial penetration of the polyethylene oxide chains of the triblock copolymer in the silica walls during the synthesis.[30,31] An overall trend shows that an increasing

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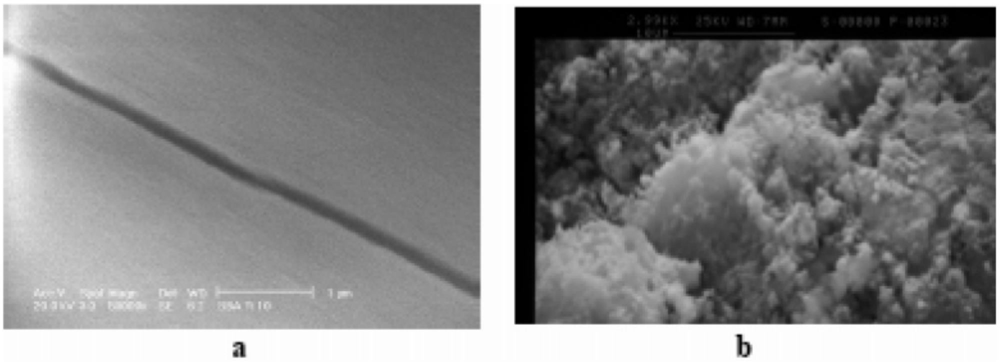

Figure 4. SEM micrographs of as-calcined samples (a) **MTi10** and (b) **MTi30**.

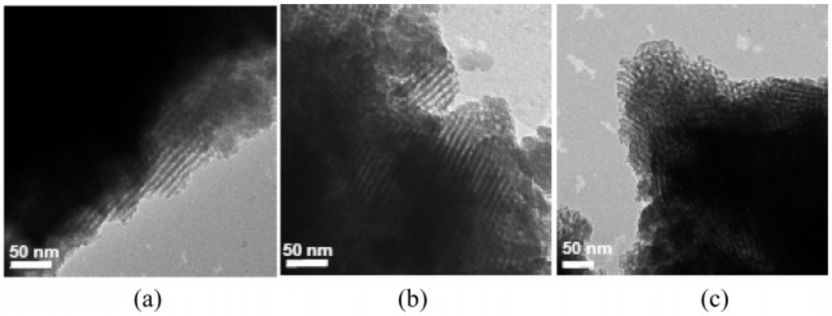

Figure 5. Transmission electron micrographs of samples (a) **MTi5**, (b) **MTi15**, and (c) **MTi30**.

amount of Ti in the sample leads to a decrease in the amount of microporosity.

The mesoporosity is characterized by the capillary condensation step in the isotherm between relative pressures of 0.5 and 0.8. No further macroporosity is detected. The capillary condensation step between p/p^0 0.5 and 0.8 is much reduced for the sample with 30 wt % Ti; however, an additional filling step at a relative pressure above 0.9 relative pressure is observed. One can speculate about this macroporosity, which is most probably due to interparticular voids, maybe between TiO_2 particles. For the other samples, the height of the capillary condensation step between p/p^0 0.5 and 0.8 does not vary significantly with titania content in the sample. However, one can note that the onset of this capillary condensation step occurs at increasing relative pressures with increasing Ti content in the sample. This indicates that the average pore size increases with increasing Ti content.

Further differences can be seen in the desorption isotherms. Samples with 10 and 15 wt % Ti show a distinct emptying of the pores in two steps. Such a phenomenon can be explained by constrictions in the pores. The more open porosity emptying in the first step leads to the pores being delimited by the constrictions, and thus they empty at lower relative pressures in the second step.

These results suggest that the introduction of up to 15 wt % titania into the synthesis leads to a decrease in the micropore volume with no influence on the mesopore volume. However, a small increase in mesopore size is observed with increasing titiania content.

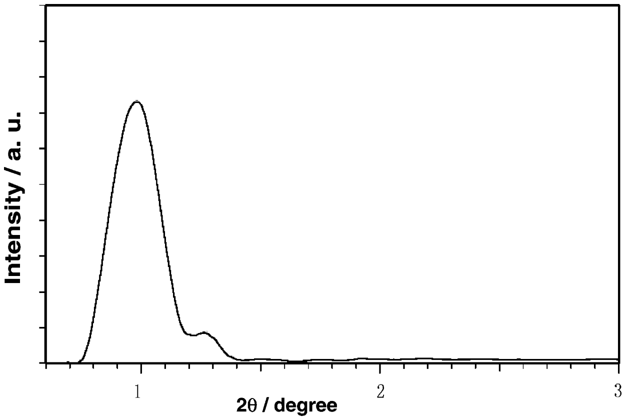

Figure 6. Low-angle X-ray pattern of the mesoporous silica.

The addition of 30 wt % titania leads to an isotherm much like that of the pure silica SBA16 with highly reduced porosity. This highlights that there still remain domains with mesoporosity of narrow pore size distribution. The adsorption at higher relative pressure suggests that the titania does not participate in the mesoporosity but may be in the form of nonporous particles creating interparticle macroporous domains in the sample.

Scanning Electron Microscopy. The differences are also in agreement with the morphology of the samples, observed by SEM. Figure 4a shows a typical scanning electron micrograph of as-calcined sample **MTi10**. The surface of the sample is very smooth, containing cracks that probably formed in the process of the drying of the gel and the calcination. On the contrary, the surface of sample **MTi30** is very rough, as evident from the SEM presented in Figure 4b. These results clearly indicate that up to a Ti:Si mass ratio equal to 15 wt %, the titania can be still be incorporated/

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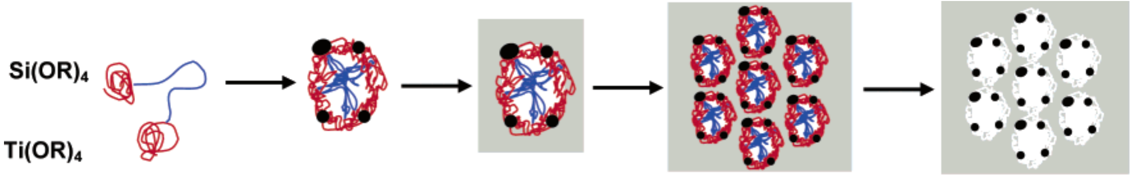
Scheme 1. Model of Formation of the TiO_2-SiO_2 Mesoporous Matrix



embedded into the mesoporous structure of the silica without its disruption.

Transmission Electron Microscopy. TEM measurements were performed on as-calcined samples **MTi5**, **MTi10**, **MTi15**, and **MTi30**. As can be shown in Figure 5, an ordered mesoporous (cubic) structure is obtained for all samples. Pore size can be estimated to be between 5 and 10 nm. All samples are very similar; there are no particles inside mesopores, but there seems to be some spherical particles at the surface of pore walls. For example, in the case of the **MTi15** sample, these particles have a diameter of about 3−5 nm.

X-ray Diffraction Study. The small-angle X-ray diffraction (XRD) pattern of mesoporous silica is shown in Figure 6. Two well-resolved diffraction peaks can be assigned to (110) and (200) diffractions for cubic space group (*Im*3*m*). The value of the cubic-cell parameter is 13.3 nm, close to that reported in the literature.[7] These results are in agreement with those obtained using TEM.

Wide-angle X-ray diffraction analysis has shown that for all as-calcined samples, no diffraction peaks of crystallized titania were observed.

Proposed Model for the Formation of Silica−Titania Mesoporous Matrix. Samples were prepared from a mixture of silica and titania precursors, a cosolvent, a template, and HCl solution. In general, the positive charge of titanium in the alkoxide precursor is significantly higher than that of the silicon in the related alkoxide. This enhances the sol−gel activity of titanium over that of silicon. This property often results in a more-rapid formation of titania building blocks compared to silica. Another key parameter for titania-based mesoporous materials prepared from block copolymers is the strength of the interactions between the metal and the structure-directing agent. These are strongly dependent on the solvent. Soler-Illia and co-workers have studied in detail the role of these interactions in the template construction of mesostructured hybrid organic−inorganic composites.[32] According to their results, if the medium contains large quantities of water and acid, it leads to several consequences. First, the presence of a large amount of water and acid blur the coordination bonds that comprise the hybrid interface, yielding weak interactions; this allows for the formation of nanosized hydrophilic building blocks of titania. Second, the difference in hydrophobicity/hydrophilicity between the PEO and PPO chains is increased at a high water content compared to a low one. Thus, segregation between both blocks is enhanced; the formation of a well-ordered mesophase is favored.[32] In addition, as reported recently by Kleitz et al. with Pluronic F127, butanol can act as a cosurfactant to modify the mesophase formation and allow an increase in the phase domains for ordered cagelike mesoporous materials with cubic symmetry.[33]

As shown in Scheme 1, small units of titania are first formed in the hydrophilic domains of the folded block copolymers; as the reaction carries on, silica units are then formed all around the preformed titania particles. A mixed-oxide TiO_2-SiO_2 mesoporous matrix is then obtained after the removal of templates, with titania particles located mainly at the surface of pore walls.

This model is confirmed by the experimental results we obtained:

(i) Adsorption measurements and TEM pictures allow us to conclude that titania is not inside the mesopores. Indeed, the total mesopore value does not vary with the amount of titania, and the mesopore diameter increases slightly. This means that for samples **MTi5−MTi15**, the whole mesostructure is not affected by the incorporation of titania. This is confirmed by a TEM experiment; all samples exhibit an organized mesosporous structure of cubic type and there is nothing inside the mesopores.

(ii) Adsorption measurements have shown that microporosity is affected by titania incorporation. It was shown for the mesoporous silica matrix that microporosity is often due to the partial penetration of poly(ethylene oxide) chains of the triblock copolymer in the silica walls during synthesis. If microporosity changes with the amount of titania, it means there is probably a change at the micelle surface mesophase. This phenomenon can be explained by the hindered Ti−polymer interactions and also by the high reactivity of titanium toward hydrolysis and condensation compared to silicon.

3.2. Thermal Stability of Mesoporous Silica Modified by Titania. *Infrared Spectroscopy.* Infrared spectra of the as-calcined samples and those thermally treated at the temperatures of 650, 850, and 1000 °C showed an evolution of the bands corresponding to Ti−O−Ti vibrations (see Figure 7). The changes in the spectra can be assigned to the decrease in the dispersion and to the growth of the TiO_2 particles. As the temperature increases, the dispersed titania is agglomerated and larger TiO_2 (anatase) molecules are formed (see TEM and XRD results). The bands around 620 cm^{-1} are typical for the vibration in the bulk TiO_2.[23]

Diffuse−Reflectance UV Spectra. Figure 2b shows UV DRS spectra of as-calcined sample **MTi5** thermally treated at 650, 850, and 1000 °C. From Figure 2b, it is obvious that the absorption edge slightly increases to higher wavelengths with increasing temperature. Particularly, the sample thermally treated at 1000 °C showed a significant shoulder at

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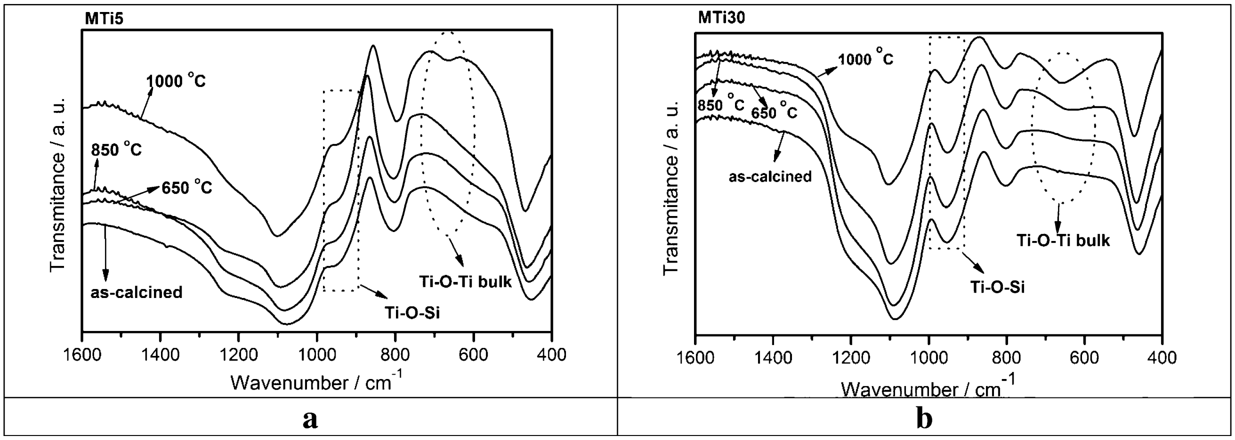

Figure 7. FT-IR spectra of samples (a) **MTi5** and (b) **MTi30** thermally treated at 550, 650, 850, and 1000 °C.

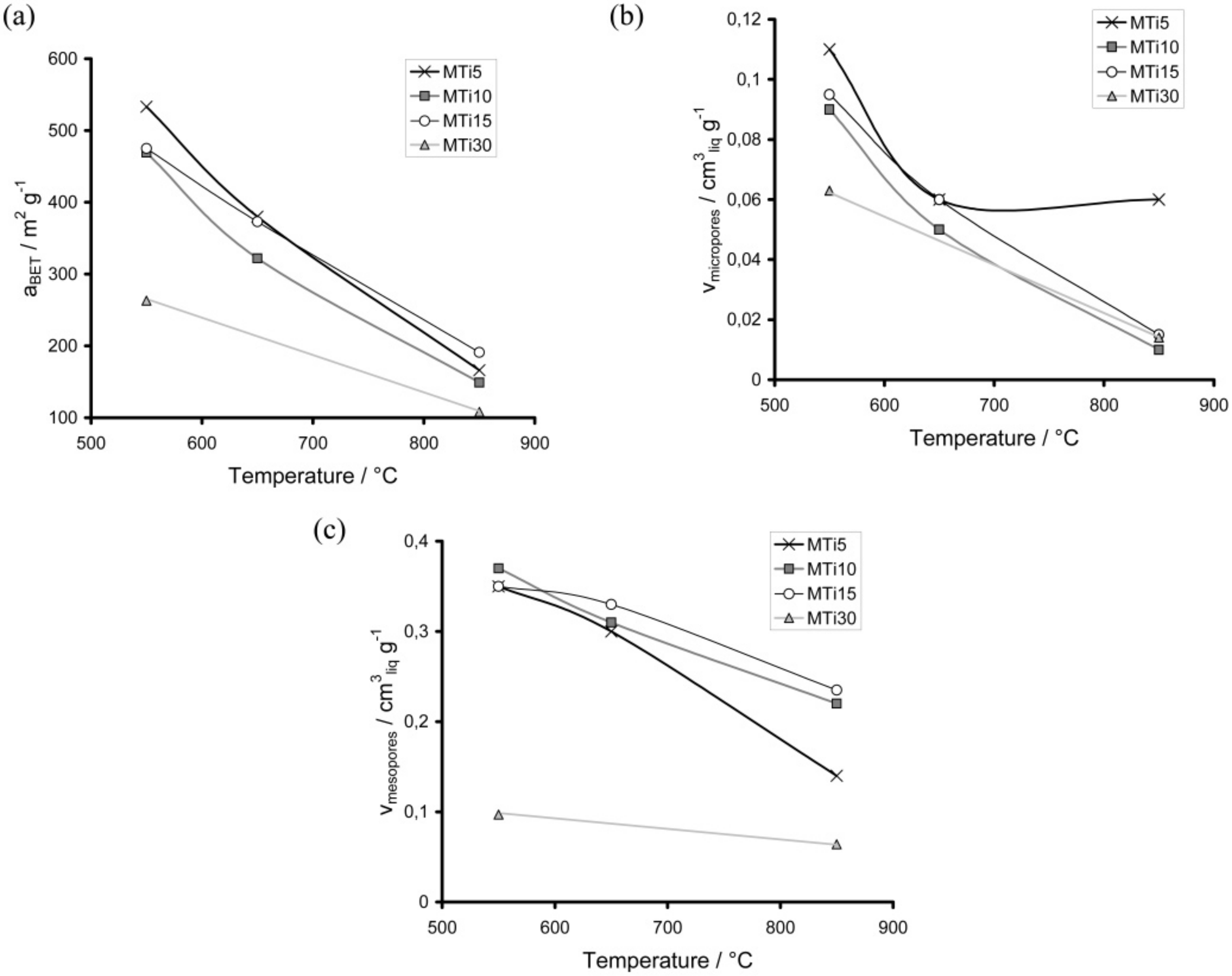

Figure 8. Evolution of (a) equivalent BET surface area, (b) micropore volume, and (c) mesopore volume with pretreatment temperature of the sample .

330 nm that is typical of ligand-to-metal charge transfer in the bulk TiO_2 anatase.[26,34,35]

Furthermore, the decrease in the absorption in the region 230−260 nm with increasing temperature was observed. This could be explained by the annealing of the surface hydroxyls, change in the hydration, and consequently a change in the coordination state of the Ti atoms.

Nitrogen Adsorption−Desorption Measurements. Figure 8 shows the evolution of (a) equivalent BET surface area, (b) micropore volume, and (c) mesopore volume with the pretreatment temperature of the sample. These volumes were calculated after *t*-plot analysis of the isotherms. The three trends on each curve correspond to the sample prepared with

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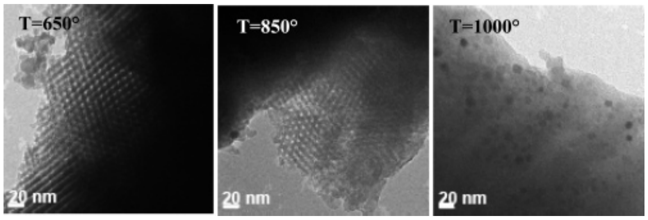


Figure 9. TEM pictures of sample **MTi5** thermally treated at different temperatures.

5, 10, 15, and 30 wt % titania.

It can be clearly seen that an increase in treatment temperature from 550 to 850 °C leads to a decrease in all of the above parameters. This suggests that the samples contract with increased treatment temperature. Even if there is an important decrease in the total surface area (a decrease of more than 60%), samples still remain mesoporous. This is in contrast with the pure silica sample, for which a collapse of the mesoporous structure was observed after heating to 800 °C. Thus, simple addition of titania enhanced the thermal stability of silica with no pore collapse below 850 °C. The higher thermal stability is of interest for the application of such materials in heterogeneous catalysis. Samples calcined at 1000 °C (not shown) are nonporous or slightly porous. Furthermore, more-important decreases in micropores volume are observed compared to those in mesopores volume, which is probably due to the crystallization and growth of the titania particles.

Transmission Electron Microscopy Experiments. TEM pictures obtained on all the different samples are shown in Figure 9. The study of the evolution of the mesoporosity with temperature by TEM permits us to observe that (i) samples **MTi5**−**MTi30** remain mesoporous up to 850 °C and (ii) samples **MTi5**−**MTi30** thermally treated at 1000 °C are nonporous or slightly porous.

The location of the TiO_2 nanoparticles is not obvious from the TEM picture of **MTi5** calcined at 650 °C, as was already mentioned in the section 3.1. Nevertheless, in the TEM picture of **MTi5** calcined at 850 °C, dark spots of diameter between 3 and 5 nm are observed at the surface of the pore walls. When the temperature reaches 1000 °C (nonporous matrix), TiO_2 nanoparticles of diameter between 5 and 10 nm are present.

X-ray Diffraction Study. The phase evolution of the titania during the thermal treatment was characterized by powder XRD. The as-calcined samples and those thermally treated at 650 and 850 °C were X-ray amorphous. For the samples calcined at 1000 °C, the diffraction peaks of crystallized TiO_2 (anatase) appeared. From these results, it follows that in SiO_2-TiO_2 composite materials, the anatase phase of titania is preserved to higher temperatures in comparison with bulk TiO_2, where the phase change from anatase to rutile takes place at significantly lower temperatures.[2,3,10]

3.3. Discussion. If we consider the model of formation proposed in the first part of the study, meaning that TiO_2 nanoparticles are located at the surface of the pore walls and surrounded by silica matrix, the evolution of the mesoporous composite with temperature can be schematically represented in Scheme 2.

The increase in temperature from 650 to 1000 °C allows for mass transport in the whole material and leads to two different processes: (i) densification, crystallization, and growth of the TiO_2 nanoparticles; or (ii) densification and collapse of the silica matrix.[36] This means that pore walls are strongly modified with temperature and that micropore and mesopore volumes decrease. Furthermore, when the temperature reaches a certain value, the thermal energy is sufficiently high to collapse the mesoporous structure.

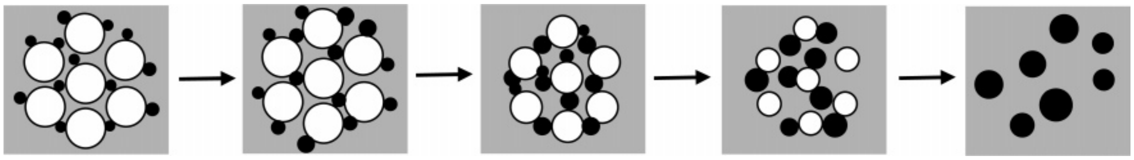
For temperature between 650 and 850 °C, nitrogen sorption measurements have shown that the micropore volume strongly decreases with increasing temperature and that this decrease is much larger than the one observed for the mesopore volume. This is in agreement with the presence of TiO_2 nanoparticles at the surface of pore walls and with their growth and densification. At the same time, the surrounded silica matrix undergoes densification and also contributes, to a lesser extent, to the decrease in microporosity. The decrease in the mesopore volume is less important because of the presence of dense TiO_2 nanoparticles at the surface of the pore walls, which probably reinforced them. Usually, the thermal treatment of a mesoporous structure (silica and titania) is always accompanied by high shrinkage of the mesoporous structure and followed by its total collapse at temperatures between 700 and 800 °C (depending on the way the matrix is synthesized). In our case, even after a thermal treatment at 850 °C, the mixed SiO_2-TiO_2 matrix remains mesoporous, as shown by the results obtained with nitrogen sorption and TEM experiments. This is in agreement with the presence of dense TiO_2 nanoparticles at the surface of the pore walls, which strengthens the whole structure. When the temperature reaches 1000 °C, the thermal energy is sufficiently high to collapse the mesoporous structure (as shown with TEM) and give rise to larger nanocrystalline TiO_2 particles. The densification, growth, and rise to the crystallization of titania nanoparticles is confirmed by TEM, IR, UV−visible, and XRD measurements.

4. Conclusion

Mesoporous silica modified with titania was prepared using the sol−gel process, i.e., starting from a mixture of titanium and silicium alkoxides and Pluronic as structure-directing agent in an aqueous acidic medium.

The resulting matrix has an ordered cubic mesoporous structure composed of small dense units of titania located at the surface of pore walls surrounded by the silica matrix. A

Scheme 2. Model of the Evolution of Mesoporous Structure with Temperature



model of formation of this material was proposed. It is based on the interaction developed between the metal atoms and the structure-directing agent, which depends strongly on the solvent. The proposed model was confirmed by experimental results (nitrogen sorption, TEM, IR and UV−visible spectra).

The thermal stability of this mixed-oxide mesoporous matrix was also investigated from 650 to 1000 °C. IR, TEM, and nitrogen sorption measurements have shown that the increase in temperature leads to the growth and densification of TiO_2 nanoparticles associated with a shrinkage of the mesoporous structure. Furthermore, the structure remains mesoporous up to 850 °C; the incorporation of titania thus leads to an increase in thermal stability compared to compounds such as pure silica or pure titania. This strengthening of the matrix is explained by the presence of dense titania nanoparticles at the surface of pore walls, which are more rigid than silica. Growth and crystallization of titania particles after thermal treatment was also shown; an anatase phase was found for titania nanoparticles at 1000 °C.

In the field of photocatalysis, these mesoporous nanocomposites can be very interesting. Indeed, TiO_2 nanoparticles are well-dispersed at the surface of the pore walls of the matrix and present an anatase phase even after a thermal treatment at 1000 °C. They may present reduced bulk defects, i.e., sites of recombination of photoexcited electron−hole pairs that are desirable for enhancing the photocatalytic activity.

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