

Anatase Formation during the Synthesis of Mesoporous Titania and Its Photocatalytic Effect

Evi Beyers,* Pegie Cool, and Etienne F. Vansant

Department of Chemistry, Laboratory of Adsorption and Catalysis, University of Antwerp (UA),
Universiteitsplein 1, B-2610 Wilrijk, Belgium

Received: January 18, 2005; In Final Form: March 31, 2005

Thermally stable mesoporous titania can be synthesized following different synthesis routes. In this paper, mesoporous titania was synthesized applying the evaporation-induced self-assembly (EISA) method. The mesostructured titania was treated with an NH_4OH solution to increase the thermal stability. The influence of this postsynthesis treatment on the anatase formation was investigated using different initial synthesis conditions. Mesoporous titania was synthesized under both acidic and basic conditions, with hexadecylamine and cetyltrimethylammonium bromide as surfactants. The samples were investigated with FT-Raman to investigate when exactly anatase was formed during the synthesis. It will be shown that the anatase formation depends mainly on the initial synthesis conditions. This study shows that anatase can already be formed before calcination under certain circumstances. Furthermore, the accessibility of the anatase phase influenced the photocatalytic activity.

Introduction

In 1992, the researchers of Mobil Oil Corporation synthesized the first ordered mesoporous silica material, MCM.¹ This investigation led to a growing interest for the development of other mesoporous materials. It would be very interesting to synthesize mesoporous transition metaloxide materials on the basis of their potential catalytic activity in various reactions. Indeed, because of the variable oxidation states and the populated d-bands of the transition metals, these materials are frequently used in catalysis, in electronic or magnetic applications, sensors, and so forth.² Of all the transition metaloxides, titania was investigated frequently because of its semiconducting possibilities and photocatalytic activity of the crystalline anatase.³ Titania is often used as photocatalyst for decolorizing wastewater^{4–7} or for the oxidation of other organic compounds.^{8,9} Anatase can decompose organic compounds, if these large organic molecules are able to reach the photocatalytic active anatase. Therefore, it is interesting to synthesize mesoporous titania, with anatase in its structure. Mesoporous materials have high surface areas and high pore volumes because of the large dimensions of the pores.

Many efforts have been performed to synthesize mesoporous titania. Researchers have used different surfactants such as alkyl phosphate anionic surfactants,^{10,11} quaternary ammonium cations,^{12,13} primary amines,^{11,14,15} and poly(ethylene)oxide-based surfactants,^{16–18} but they all have to overcome one of the major drawbacks in the synthesis of mesoporous titania, namely, the high reactivity of the initial titanium compounds toward hydrolysis and condensation. If this high reactivity is not tempered, a poorly organized structure will be formed. The high reactivity of the precursors can be efficiently controlled by pH adjustment and complexation effects. In most of the syntheses, a controlled amount of water is added to a nonaqueous solvent, leading to a specific formation of the mesoporous structure. Such

a combination was first reported by Stucky et al.¹⁷ They used a poly(ethylene)oxide (PEO)-based surfactant and dissolved it in a nonaqueous medium (ethanol). The acidic medium was generated during the synthesis by the addition of a chloride precursor, resulting in a sol, which was transferred in an open Petri dish for gelating. This method was extended by Sanchez et al.¹² to ionic cetyltrimethylammonium (CTA^+) templates. They called this method evaporation-induced self-assembly EISA-method, because the self-assembly occurred during the controlled solvent evaporation, leading to an incomplete polymerized inorganic network. Further polymerization of the network is necessary and is often done by a thermal treatment.

This thermal treatment or calcination process often results in a collapse of the mesoporous structure. By the thermal removal of the surfactant, the amorphous titania crystallizes, but mostly resulting in a poor mesoporous structure. A possible solution is the use of extractable surfactants such as amines¹⁴ and poly(ethylene)oxide-based surfactants.¹⁹ This results in amorphous structures, which are not usable for photocatalytic reactions, where anatase is the catalytic active phase. The use of poly(ethylene)oxide-based surfactants results in structures with thicker walls, wherein crystallization can accommodate more easily^{17,20} giving rise to mesoporous structures with a higher thermal stability. Another method to create mesoporous titania structures with thicker walls is developed by Tatsumi et al.¹⁴ Mesoporous titania structures were prepared, using the extractable primary amines as structure-directing agent. After extraction of the surfactant with *p*-toluene sulfonic acid, titanium-isopropoxide was deposited on the surface by use of chemical vapor deposition, followed by its decomposition with water vapor. Chemical vapor deposition of titania increases the wall thickness, resulting in thermally more stable materials.

Other methods, increasing the thermal stability of mesoporous titania, consist of the introduction of a stabilization step during the synthesis, before calcination. Herrmann et al.²¹ doped the mesoporous titania with sodium oxide. In this synthesis, sodium hydroxide was used to remove introduced phosphate groups.

* To whom correspondence should be addressed. E-mail: evi.beyers@ua.ac.be; fax: +32-3-820.23.74; tel: +32-3-820.23.54.

Calcination at 350 °C resulted in sodium oxide doped mesoporous titania. This material has a higher thermal stability than the undoped analogues. Furthermore, it was observed that the temperature at which the structure collapses shifts to higher values with increasing sodium content.

Recently, a postsynthesis treatment of mesoporous titania with NH_3 was found to be of great importance to increase the thermal stability of mesoporous titania and other transition metal-oxides.^{18,22–24} This postsynthesis method can be carried out in the gaseous or liquid phase. The method was first developed by Sanchez, who successively treated deposited titania films under NH_3 atmosphere, resulting in structures stable up to 350 °C.¹⁸ This method was further optimized to mesoporous titania powders, which were treated with an aqueous NH_4OH -solution.^{22,24} The titania-hybrid is refluxed in an NH_4OH -solution, during 2 days at pH 9–10, resulting in a thermally stable (600 °C) mesoporous titania structure with anatase nanoparticles in the walls.

In this study, the postsynthesis treatment with an NH_4OH -solution has been applied on various titania powders, prepared by using different initial synthesis conditions. Mesoporous titania is synthesized in acidic and basic medium with different surfactants, resulting in materials where at different moments in the synthesis anatase is formed. The effect of this anatase formation on the photocatalytic activity was also investigated.

Experimental Section

Synthesis. For the synthesis of mesoporous titania, hexadecylamine (HDA; Acros 90%) or cetyltrimethylammoniumbromide (CTABr; Acros 90%) was used as surfactants, while titanium tetra-isopropoxide ($\text{Ti}(\text{O}^i\text{Pr})_4$; Aldrich 97%) was used as a titanium source.

Method I. The samples were synthesized following a method deduced from the EISA-procedure¹⁸ with different surfactants.²⁴ The EISA-procedure was used with CTABr as surfactant in the following way: $\text{Ti}(\text{O}^i\text{Pr})_4$ was added to an ethanolic HCl (Acros pro analysis grade) solution, resulting in a titanium precursor solution, which was added to an ethanolic CTABr solution. After vigorous stirring, the resulting solution was transferred into an open Petri dish for 7 days at 60 °C to evaporate the solvent. The molar ratios were $\text{Ti}:\text{CTABr}:\text{HCl}:\text{H}_2\text{O}:\text{EtOH} = 1:0.16:1.4:17:20$. This method was only used with CTABr as surfactant. Samples synthesized in this way were denoted $\text{TiO}_2\text{-CTABr}$.

Method II. Mesoporous titania was also synthesized with HDA, with or without the addition of concentrated HCl. After dissolution of HDA in EtOH, $\text{Ti}(\text{O}^i\text{Pr})_4$ was added and stirred at ambient temperature. After a dropwise addition of water to this solution, a white suspension was formed and the mixture was stirred for 15 min. If HCl was added to the ethanolic HDA solution, no suspension was formed immediately after water addition. Both solutions are further treated the same way. The solutions were aged at room temperature in a closed system to avoid evaporation. The molar gel composition was $\text{Ti}:\text{HDA}:\text{H}_2\text{O}:\text{EtOH}:(\text{HCl}) = 1:0.33:2:90:(0.6)$. After 24 h aging, the mixture was transferred into a Petri dish for 7 days at room temperature to evaporate the solvent. Samples synthesized in this way were denoted $\text{TiO}_2\text{-HDA-A-T}$ and $\text{TiO}_2\text{-HDA-B-T}$. Samples with CTABr as surfactant were also synthesized following method II under both acidic and basic conditions, further denoted, respectively, $\text{TiO}_2\text{-CTABr-A-T}$ and $\text{TiO}_2\text{-CTABr-B-T}$.

All mesostructured titania samples were NH_3 -treated for 48 h in a reflux system. One gram of solid was treated with 50 mL of basic water. The pH was kept constant between a value

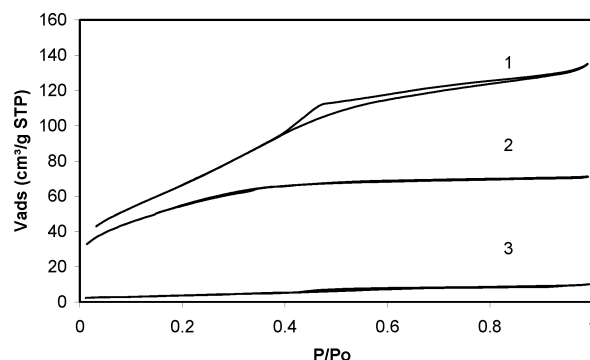


Figure 1. N_2 -adsorption-desorption isotherms at 77 K $\text{TiO}_2\text{-HDA-A-T}$ (1) and $\text{TiO}_2\text{-HDA-B-T}$ (2) and $\text{TiO}_2\text{-HDA-NT}$ (3).

of 9 and 10, by the addition of NH_4OH (Acros 28–30% p.a.). After the NH_3 -treatment, all samples were calcined during 2 h at 300 °C in a tube furnace, under air flow.

Characterization. For all samples, the surface area and the porosity were determined on a Quantachrome Autosorb-1-MP automated gas adsorption system. Prior to the N_2 -adsorption, all the samples were outgassed at 200 °C for 16 h. The N_2 -adsorption was carried out at liquid nitrogen temperature (77 K). FT-Raman was used to determine the crystal phases in the titania structure. Samples were measured on a Nicolet Nexus 670 bench equipped with a Ge detector in a 180° reflective sampling configuration using a 1064 nm Nd:YAG laser.

Catalysis. The photocatalytic activity of the samples (25 mg of photocatalyst) was tested by the decomposition of rhodamine 6G solution (25 mL with initial concentration 4×10^{-5} M). Prior to irradiation, the sample was magnetically stirred for 30 min to establish an adsorption-desorption equilibrium, between the catalyst surface and the dye. Afterward, the solution was irradiated with a 100 W Hg lamp (Sylvania Par 38). The concentration of remaining rhodamine 6G was analyzed every 10 min by UV-vis spectroscopy using a Unicam 8700 spectrometer.

Results and Discussion

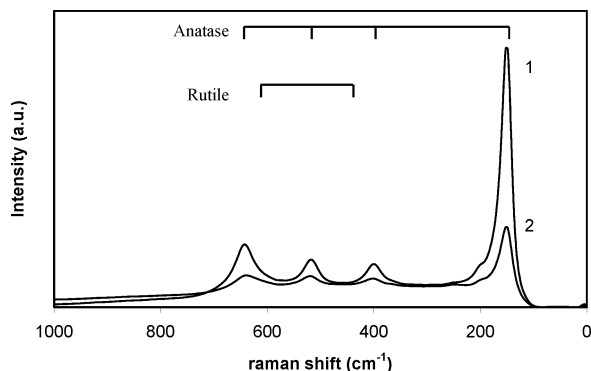
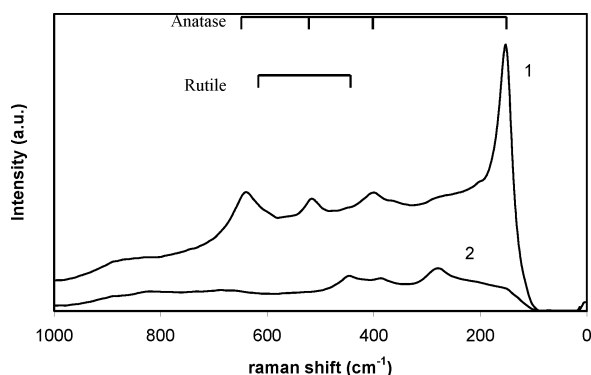
a. Synthesis. Mesoporous titania synthesized under basic conditions with a primary amine, hexadecylamine, as structure-directing agent shows different crystalline phases as a function of the calcination temperature. This is in agreement with previously published data, reported on the stabilizing effect of NH_3 -treatment on mesoporous titania.²⁴ Therein mesoporous titania was synthesized with HDA as surfactant under basic conditions. For nontreated mesoporous titania, anatase was formed between 350 °C and 400 °C, whereas for the NH_3 -treated samples a temperature of 300–350 °C was required to detect anatase. However, in this study, mesoporous NH_3 -treated titania was synthesized with CTABr, following method I of the experimental part ($\text{TiO}_2\text{-CTABr}$). This method led to mesoporous structures, wherein anatase is already formed at room temperature. This difference must be explained by the synthesis procedure. There are two main differences, namely, the utilized surfactant and the medium in which the synthesis was carried out.

To avoid the role of the nature of the surfactants, samples were made by using HDA as surfactant in a basic and an acidic medium. Figure 1 shows the N_2 -adsorption-desorption isotherms at 77 K of the NH_3 -treated samples synthesized under acidic and basic conditions as well as a nontreated sample. It is obvious that calcination of a nontreated sample leads to the loss of its mesoporous structure, where the NH_3 -treated samples retain their mesoporosity. This indicates that an NH_3 -treatment is necessary

TABLE 1: Physical Characteristics of Mesoporous Titania NH₃-Treated and Nontreated Synthesized with HDA and CTABr in Acidic (A) and Basic (B) Medium, Derived from N₂-Sorption Measurements at 77 K

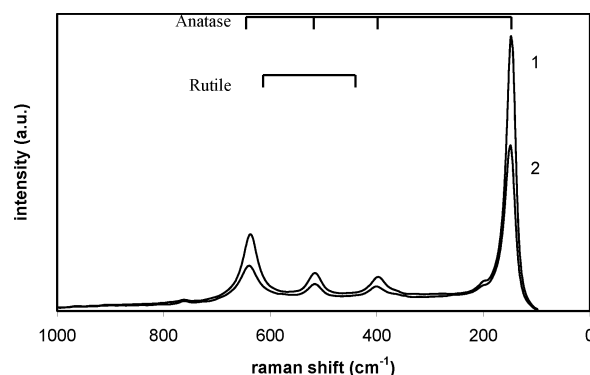
sample ^a	<i>S</i> _{BET} (m ² /g)	<i>V</i> _p (cm ³ /g)	<i>D</i> _{BJH} (Å)
TiO ₂ -HDA-A-T	258	0.20	26.8
TiO ₂ -HDA-B-T	195	0.11	20.0
TiO ₂ -HDA-NT	13	0.01	<i>b</i>
TiO ₂ -CTABr-A-T	340	0.28	34.0
TiO ₂ -CTABr-B-T	180	0.25	32.0(broad)

^a T stands for NH₃-treated and NT for nontreated with NH₄OH. ^b No capillary condensation step was observed in the N₂ isotherm.

**Figure 2.** FT-Raman spectra of TiO₂-HDA-A-T (1) and TiO₂-HDA-B-T (2) after calcination.**Figure 3.** FT-Raman spectra of TiO₂-HDA-A-T (1) and TiO₂-HDA-B-T (2) before calcination.

for the stabilization of the mesoporous structure. The samples synthesized under acidic conditions have a higher surface area and pore volume compared to those synthesized under basic conditions (Table 1). It is obvious that under acidic conditions a better structured mesoporous titania can be formed. This observation can be attributed to the tempering effect of the acidic medium on the condensation rate of titania.

FT-Raman spectra were measured in three different stadia of the synthesis procedure. FT-Raman spectra were measured on samples without NH₃-treatment and before and after calcination of the NH₃-treated samples, synthesized in acidic and basic medium. The samples without NH₃-treatment were measured before calcination with FT-Raman. Both samples, synthesized in acidic or basic medium, are amorphous before calcination (spectra not shown). Upon calcination, both samples transformed into anatase with the loss of their mesoporous structure (see Figure 1). The FT-Raman spectra of the NH₃-treated samples after calcination show for both samples anatase bands (Figure 2). Figure 3 represents the FT-Raman spectra of the NH₃-treated sample, before calcination. There is a clear difference between the spectrum of the sample synthesized in acidic medium and

**Figure 4.** FT-Raman spectra of TiO₂-CTABr-B-T (1) and TiO₂-CTABr-A-T (2) before calcination.

the one synthesized in basic medium. When the sample is synthesized in acidic medium, it already contains anatase before calcination, whereas samples synthesized in basic medium show no anatase phase. Therefore, different synthesis conditions will lead to structures where anatase is formed at different moments in the synthesis procedure. In basic medium, anatase is only formed during calcination.

A possible explanation for this different mechanism of the anatase formation can be found in the initial synthesis conditions, namely, the medium in which the synthesis is carried out. Indeed, titania has a different condensation rate in an acidic and in a basic medium. The condensation of titania in acidic medium is much slower than that in a basic medium, because an acidic medium is known to slow the reactivity of the titania precursor.²⁵ In an acidic medium, titania condensates during the evaporation of the solvent, where in a basic medium titania immediately condensates with the addition of water. This was clearly observed during the experiment, because in a basic medium a white suspension was formed immediately after the addition of water, where in acidic medium the solution remained clear upon water addition. This fast condensation under basic conditions probably leads to arbitrary bondings, resulting in a strongly condensed but poorly defined structure. Further NH₃-treatment of these samples cannot organize the structure into a crystalline structure. Anatase is only formed upon calcination. In contrast, samples prepared in acidic medium result probably in less condensed structures. NH₃-treatment of the samples condensates these samples further, resulting in the formation of anatase in the walls even at room temperature.

Mesoporous titania was also synthesized using CTABr as the surfactant in acidic and basic medium, following the synthesis procedure of HDA (method II of the experimental part). FT-Raman spectra were measured of the NH₃-treated samples before calcination (Figure 4). In acidic medium, anatase was already formed before calcination. This was in agreement with the results found for materials synthesized with HDA in acidic medium (Figure 3). However, using CTABr under basic conditions gives rise to the formation of anatase before calcination. This means that the moment of anatase formation can not only be explained by the medium used, because the type of surfactant seems to also have an influence. Therefore, the condensation rate of titania does not only depend on the medium used but also on the nature of the surfactant.

The use of different surfactants under the same conditions results in a different moment on which the anatase is formed during the synthesis procedure. A possible explanation has to be found in the differences in interactions between the titania and the surfactant. The interactions between the surfactants and titania are presented in Figure 5. In basic medium, titania is

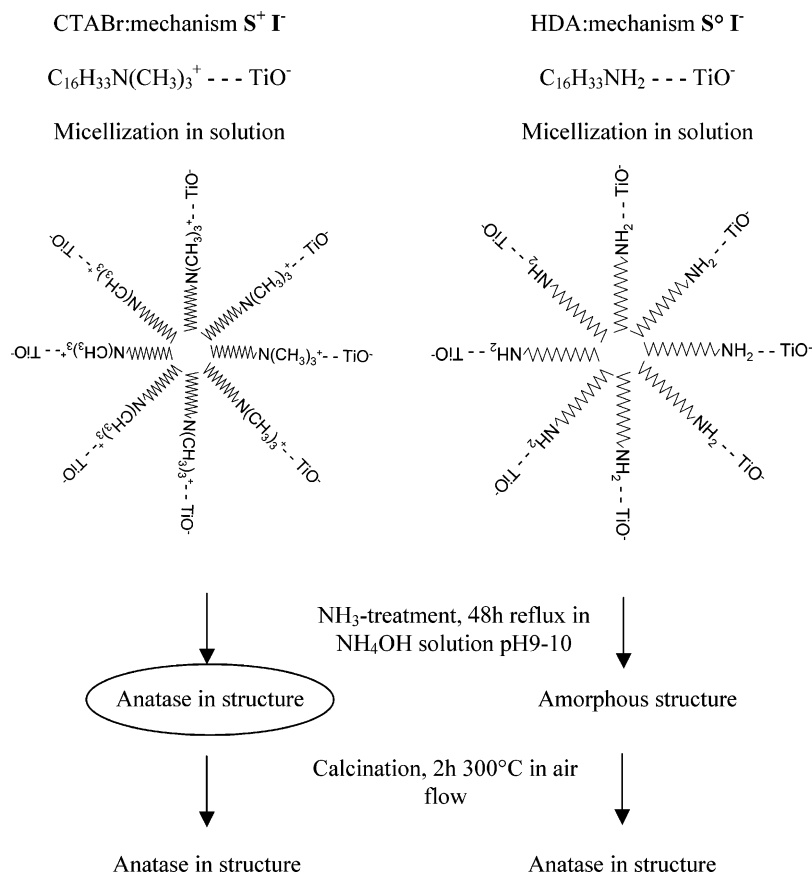


Figure 5. Schematical presentation of the interactions occurring during the synthesis.

negatively charged, because the pH is higher than the isoelectric point of titania. The difference in interactions between titania and the surfactants is due to the different charges on the surfactants. CTABr is always positively charged, independently of the medium used, resulting in a S^+I^- interaction mechanism. In contrast, the charge of HDA depends on the pH. The degree of protonation of HDA as a function of the pH can be calculated on the basis of the pK_a -value. It is clear that when HDA is used under basic conditions, HDA is not protonated. This results in a S^0I^- interaction mechanism when HDA is used as a surfactant.

As a consequence, the interaction between CTABr and titania under basic conditions can be ascribed to a real electrostatic interaction, where the interaction between HDA and titania reveals a hydrogen-bonding interaction. The strong interaction between titania and CTABr results in a less strong interaction between neighboring titania particles, leading to a less condensed state of the mesostructured titania before the NH_3 -treatment. In contrast, the weak hydrogen-bonding interaction between HDA and titania makes a strong interaction and condensation between mutual titania particles possible. This will lead to a strong condensed titania network in a poorly defined structure, with a lot of arbitrary bondings. After 7 days of evaporation, the samples are treated with an NH_4OH solution. During this treatment, the mesostructured titania will further condensate and consolidate. This condensation and consolidation is different for different surfactants, because those samples already have a different condensed state. Because of the low condensation between titania particles, when CTABr is used as surfactant, the NH_3 -treatment can condensate the titania particles into an anatase containing mesoporous structure. In contrast, titania synthesized with HDA is already in a very condensed state before the NH_3 -treatment, so that a NH_3 -treatment will not result in anatase formation before calcination (high temperatures).

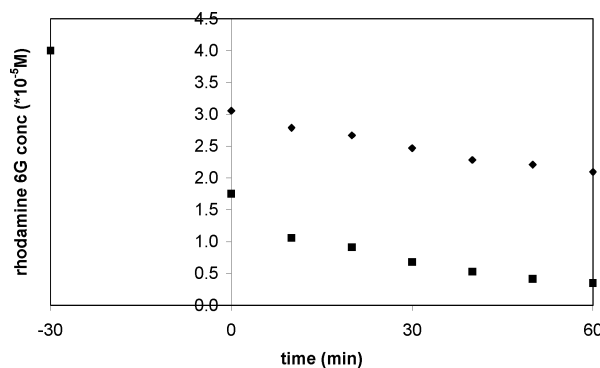


Figure 6. Catalytic performances of calcined TiO_2 -HDA-B-T (♦) and TiO_2 -CTABr-B-T (■) for photocatalytic degradation of rhodamine 6G.

b. Catalysis. Samples synthesized with HDA or CTABr under basic conditions led to structures where the latter anatase was already formed during the synthesis. Using CTABr as a surfactant led to a structure where anatase was formed before calcination. The photocatalytic activity of both types of samples was investigated by the decomposition of rhodamine 6G.

Figure 6 shows the photocatalytic degradation of rhodamine 6G for samples synthesized with HDA and CTABr in basic medium (following method II of the experimental part). The negative time scale presents the time period, where the solution was not irradiated with UV-light. During this period, the dye could not be decomposed, because anatase needs UV-light for its catalytic activity. (band gap 3.2 eV, $\lambda < 380$ nm).^{26,27} As a result of the absence of UV-light, the decrease of rhodamine 6G concentration is due to the adsorption of the dye on the surface of the titania sample. There is a clear difference in adsorption on the sample prepared with HDA and the one

TABLE 2: Calculated Rate Constants Derived from the First-Order Photocatalytic Reaction

sample	k (min ⁻¹)
TiO ₂ -HDA-A-T	0.016
TiO ₂ -HDA-B-T	0.007
TiO ₂ -CTABr-A-T	0.029
TiO ₂ -CTABr-B-T	0.029

prepared with CTABr. If titania was synthesized using CTABr, more rhodamine 6G was adsorbed. This can be explained by the different physical characteristics of both samples, summarized in Table 1. The difference between these samples is the pore diameter and as a consequence the pore volume too. The pores of the sample synthesized with CTABr are larger than those of the sample synthesized with HDA. Therefore, the large rhodamine 6G-molecules can better reach the whole surface of the CTABr sample, in contrast with the HDA sample, where the accessibility is more limited by the smaller pores.

At time 0, the solution was irradiated with UV-light. During 1 h, the photocatalytic decomposition of the solution was followed. The concentration decrease is larger for the CTABr sample than for the HDA sample. This difference is also due to the accessibility of the anatase phase. The higher photocatalytic activity of TiO₂-CTABr-B-T compared to TiO₂-HDA-B-T can also be seen in the rate constants derived from the first-order reaction kinetics ($-\ln c/c_0 = kt$). These values are summarized in Table 2. Table 2 also contains the rate constants for the photocatalytic activity of the samples synthesized under acidic conditions following method II of the experimental part (TiO₂-CTABr-A-T and TiO₂-HDA-A-T). There is no difference for the samples synthesized with CTABr as surfactant, but the activity of TiO₂-HDA-A-T is clearly higher than the activity of TiO₂-HDA-B-T. This difference can be explained by the difference in textural parameters. As Table 1 shows, the pore diameter and surface area of TiO₂-HDA-A-T are larger than those of TiO₂-HDA-B-T. The acidic medium results in a better formed structure, because of the slower condensation of titania under these conditions compared to the condensation rate under basic conditions. This better formation of the mesoporous structure leads to a better accessibility of the anatase phase, resulting in a higher photocatalytic activity of TiO₂-HDA-A-T.

The total removal of rhodamine 6G is larger for the sample synthesized with CTABr than when HDA was used as surfactant, because of the larger pores of the formed mesoporous structure. The accessibility of titania synthesized with HDA as surfactant could be increased by the addition of HCl. The acidic medium resulted in a better formed and better accessible mesoporous structure, because of the slower condensation of titania in acidic medium. In conclusion, the accessibility of the anatase phase for rhodamine 6G determines the photocatalytic activity of the mesoporous titania and can be influenced by changing the surfactant or the medium in which the synthesis was carried out.

Conclusion

Mesoporous titania has been synthesized with different surfactants under different synthesis conditions using the EISA-method, followed by an NH₃-treatment. The moment of the anatase formation during the synthesis depends on the type of surfactant and the medium and has been investigated by FT-Raman. Under acidic conditions, anatase is already formed before calcination because of the slower condensation rate of

titania under acidic conditions compared to basic conditions. Under basic conditions, titania was synthesized with HDA and CTABr, leading to a different interaction between the surfactant and titania. The strong electrostatic interaction between CTABr and titania leads to a less condensed titania structure. Further condensation of this structure during NH₃-treatment gives rise to the formation of anatase nanoparticles in the walls. The weak hydrogen-bonding interaction between HDA and titania resulted in a strongly condensed, poorly defined structure. The NH₃-treatment cannot further organize this strong condensed structure into a mesoporous structure with anatase nanocrystals in the wall.

The influence of the moment of anatase formation during the synthesis procedure on the photocatalytic activity was investigated by the decomposition of rhodamine 6G. Using CTABr as surfactant under basic conditions leads to a structure with higher photocatalytic activity than structures synthesized with HDA under the same conditions. This higher activity could be explained by the better accessibility of the anatase. The photocatalytic activity of mesoporous titania synthesized with HDA as surfactant could be increased by changing the synthesis medium from basic to acidic conditions. The slower condensation of the titania precursor lead to better formed mesoporous structure, with better accessibility for photocatalysis.

Acknowledgment. P. Cool acknowledges the FWO-Flanders (Fund for Scientific Research-Flanders) for financial support.

References and Notes

- (1) Kresge, C. T.; Leonowics, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, 359, 710.
- (2) He, X.; Antonelli, D. *Angew. Chem., Int. Ed.* **2002**, 41, 214.
- (3) Fujishima, A.; Rao, T. N.; Tryk, D. A. *J. Photochem. Photobiol., C* **2000**, 1, 1 (and references therein).
- (4) Legrini, O.; Oliveros, E.; Braun, A. M. *Chem. Rev.* **1993**, 93, 671.
- (5) Awati, P. S.; Awate, S. V.; Shah, P. P.; Ramaswamy, V. *Catal. Commun.* **2003**, 4, 393.
- (6) Sökmen, M.; Ozkan, A. *J. Photochem. Photobiol., A* **2002**, 147, 77.
- (7) Chen, J.; Liu, M.; Zhang, L.; Zhang, J.; Jin, L. *Water Res.* **2003**, 37, 3815.
- (8) Andersson, M.; Osterlund, L.; Ljungström, S.; Palmqvist, A. *J. Phys. Chem. B* **2002**, 106, 10647.
- (9) Ohno, T.; Tokieda, K.; Higashida, S.; Matsumura, M. *Appl. Catal., A* **2003**, 244, 383.
- (10) Antonelli, D. M.; Ying, J. Y. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 2014.
- (11) Dai, Q.; Zhang, Z.; He, N.; Li, P.; Yuan, C. *Mater. Sci. Eng., C* **1999**, 8–9, 417.
- (12) de A. A. Soler-Illia, G. J.; Louis, A.; Sanchez, C. *Chem. Mater.* **2002**, 14, 750.
- (13) Cabrera, A.; El Haslouri, J.; Beltrán-Porter, A.; Beltrán-Porter, D.; Marcos, M. D.; Amoros, P. *Solid State Sci.* **2000**, 2, 513.
- (14) Yoshitake, H.; Sugihara, T.; Tatsumi, T. *Chem. Mater.* **2002**, 14, 1023.
- (15) Wang, Y.-Q.; Chen, S.-G.; Tang, X.-H.; Palchik, O.; Zaban, A.; Koltypin, Y.; Gedanken, A. *J. Mater. Chem.* **2001**, 11, 521.
- (16) Alberius, P. C. A.; Frindell, K. L.; Hayward, R. C.; Kramer, E. J.; Stucky, G. D.; Chmelka, B. F. *Chem. Mater.* **2002**, 14, 3284.
- (17) Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Nature* **1998**, 396, 152.
- (18) Grosso, D.; de A. A. Soler-Illia, G. J.; Babonneau, F.; Sanchez, C.; Albouy, P.-A.; Brunet-Bruneau, A.; Balkenende, A. R. *Adv. Mater.* **2001**, 13, 1085.
- (19) Blin, J.-L.; Léonard, A.; Yuan, Z.-Y.; Gigot, L.; Vantomme, A.; Cheetham, A. K.; Su, B.-L. *Angew. Chem., Int. Ed.* **2003**, 42, 2872.
- (20) Crepaldi, E. L.; de A. A. Soler-Illia, G. J.; Grosso, D.; Sanchez, C. *New J. Chem.* **2003**, 27, 9.
- (21) Li, Q.; Härter, P.; Xue, W.-M.; Zuo, J.-L.; Herrmann, W. A. *J. Chem. Soc., Dalton Trans.* **2001**, 2719.
- (22) Cassiers, K.; Linssen, T.; Meynen, V.; Van Der Voort, P.; Cool, P.; Vansant, E. F. *Chem. Commun.* **2003**, 1178.

(23) Cassiers, K.; Linssen, T.; Aerts, K.; Cool, P.; Lebedev, O.; Van Tendeloo, G.; Van Grieken, R.; Vansant, E. F. *J. Mater. Chem.* **2003**, *13*, 3033.

(24) Cassiers, K.; Linssen, T.; Mathieu, M.; Bai, Y. Q.; Zhu, H. Y.; Cool, P.; Vansant, E. F. *J. Phys. Chem. B* **2004**, *108*, 3713.

(25) Kung, H. H.; Ko, E. I. *Chem. Eng. J.* **1996**, *64*, 203.

(26) Linsebigler, A. M.; Lu G.; Yates, J. T., Jr. *Chem. Rev.* **1995**, *95*, 735

(27) Dvoranová, D.; Brezová, V.; Mazúr, M.; Malati, M. A. *Appl. Catal., B* **2002**, *37*, 91.