

SYNTHESIS OF MESOPOROUS TITANIA IN RUTILE PHASE WITH PORE-STABLE STRUCTURE

J. G. dos Santos¹, T. Ogasawara² and R. A. Corrêa^{1*}

¹Instituto de Engenharia Nuclear, DIQN/SETEQ, Comissão Nacional de Energia Nuclear,
Phone: + (55) (21) 2173-3700, Fax: + (55) (21) 2590-2692, Cx P 68550, CEP: 21941-972,
Cidade Universitária, Ilha do Fundão, Rio de Janeiro - RJ, Brasil.

E-mail: racorrea@ien.gov.br

²Universidade Federal do Rio de Janeiro, Centro de Tecnologia,
COPPE/PEMM, Rio de Janeiro - RJ, Brasil.

(Submitted: August 19, 2008 ; Revised: December 5, 2008 ; Accepted: January 22, 2009)

Abstract - Metastable-to-stable transformation in oxides is always associated with drastic reduction in surface area and/or porosity. Therefore, all earlier efforts to stabilize the pore structure of oxides undergoing a metastable-to-stable phase transformation are interesting for both scientific and technological concerns. This work presents a new experimental technique for catalytic oxide production through sonication in acid solution for attainment of the anatase-rutile transformation. Mesoporous structure of titania and surface area were stabilized in the rutile phase after calcinations at 430 and 730°C. Analysis by scanning electron microscopy (SEM) and nitrogen isotherms showed that the mesoporous structure was preserved after calcinations. After the sonication of titania for 32 hours, rutile phase was obtained at 730°C and still kept a surface area of 28m²/g. When sonicated for 64 h, rutile was obtained at 430°C, still preserving an area of 52m²/g.

Keywords: Titania; Rutile; Mesoporous; Sonication

INTRODUCTION

Synthetic titanium dioxide can be used in a diversity of applications, as pigment or support for catalysts. Filters, ceramics, paper industry, feeding, cosmetics and staple fibers are some of the wide variety of commercial applications for TiO₂. Titania exists in three basic crystalline phases: rutile, anatase (which are commercially produced) and brookite. Each structure shows different physical properties, such as refractive index and chemical and photochemical reactivity. Each application usually requires specific crystalline structure and size of the primary particle.

New processes for synthesis of titania have been investigated to obtain nanoparticles of TiO₂ with properties specific to these different applications. Ultrasound has become an important tool in nanocrystalline synthesis. It has shown very rapid growth in its application to materials science due to its unique reaction effects (Yang et al., 2003). Recently, use of cavitation in the synthesis process has yielded smaller particle size for a variety of oxides.

Zhang and Reller (2002) demonstrated that some properties of pure and doped titania are very sensitive to changes in crystallinity. Besides the crystalline structure, particle size and surface area

*To whom correspondence should be addressed

strongly influence catalytic activity. For example, the rutile phase is very efficient for the catalysis of decomposition of H_2S ; however, the anatase phase is more effective in many other catalytic processes (Zhang, and Reller, 2003).

Thermal stability of mesoporous structures is a critical parameter for application of catalysts. The mesoporous TiO_2 , presents better performance as catalyst, due to easier accessibility of bigger molecules to the internal canals.

EXPERIMENTAL

The hydrated titanium dioxide used in this work was obtained by the hydrometallurgical route after leaching of ilmenite and the resulting solution purified by solvent extraction (Cunha and Silva, 2007).

Three TiO_2 powders of hydrated titanium dioxide were used in these studies: i) sample A – hydrated titanium dioxide obtained by slow addition of the precipitation agent (Ammonium hydroxide); ii) sample B – hydrated titanium dioxide obtained by the fast addition of the precipitation agent (Ammonium hydroxide); iii) sample C – hydrated titanium dioxide obtained from titanium sulfate solution by fast addition of the precipitation agent (Ammonium hydroxide).

Sample A was calcined at 600, 700, 800, 940, 970, and 980°C with different process times in order to study the temperature of anatase-rutile transformation. X-ray diffraction (XRD) and surface area analysis were performed before and after calcinations at different temperatures. XRD patterns were obtained in a Rigaku Miniflex Model device.

Measurements of surface area were done using the BET method in a Micromeritics GEMINI 2375 equipment. SEM for morphologic analysis was performed with a ZEISS MODEL DMS 950. Before the calcinations, amorphous titanium hydroxide was also submitted to a previous sonication with a high intensity ultrasonic field in acid solution with different periods and concentrations. The equipment used for sonication was an ultrasonic bath (THORNTON - INPEC ELETRÔNICA S.A. Model 12D, 8 L, 900W and frequency of 25kHz).

RESULTS AND DISCUSSION

To elucidate the accurate temperature of anatase-rutile transformation, tests of calcinations were carried out at 600, 700, 800, 870, 940 and 970°C for 3 hours and at 980°C for 4 hours. The results show that no anatase-rutile transformation was detected for 3 h of calcinations at 970°C (Figure 1). The Figure 2 shows the XRD patterns obtained for calcinations at 980°C, considering different periods.

The XRD patterns show that the rutile phase starts to form only at 980°C. After 4 hours, rutile is the unique phase present.

Figure 3 shows the variation of surface area with the temperature of calcinations for the two powders (sample A and B). Sample B shows a larger value of surface area due to faster precipitation. The results of Figure 3 show that surface area decreases inversely with the temperature of calcinations. For rutile conversion, surface area falls drastically to values lower than unity despite the initial value of surface area.

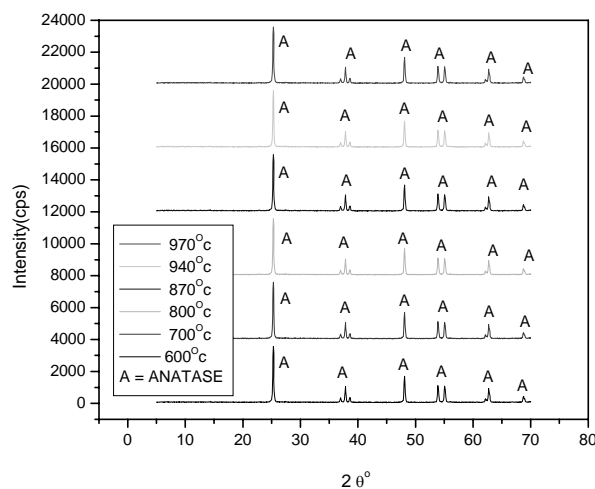


Figure 1: XRD patterns of TiO_2 anatase. Calcined for 3h at 600, 700, 870, 940 and 970°C.

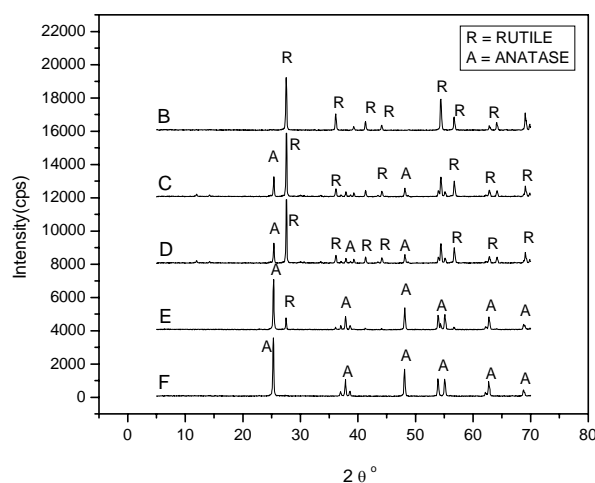


Figure 2: XRD patterns of TiO_2 . Calcinations at 980°C . 4h (B), 3h(C), 2h (D), 1h (E) and 0.5 hours (F)

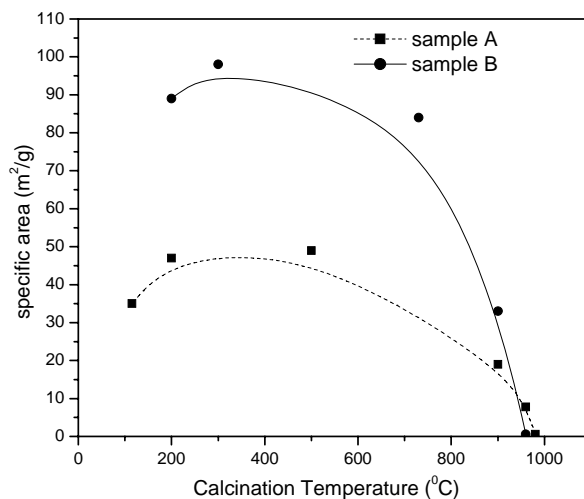


Figure 3: BET surface area vs. calcination temperature of hydrated TiO_2 without sonication.

Figures 4 and 5 illustrate clearly the influence of sonication treatment on the anatase-rutile kinetic transformation and surface area, respectively. The amount of each crystalline phase in any titania sample can be quantified from diffraction experiments. The phase content of rutile and anatase in the sample were calculated by choosing the most intense anatase and rutile peaks and observing the ratio between them as in the method used by Spurr and Mayers (1957).

While material that had not been treated was completely converted to rutile only near 1000°C , materials submitted to sonication treatment had their texture, porosity, reactivity and surface morphology changed, and the transformation temperature

occurred at lower values.

Figure 6 shows adsorption isotherms of nitrogen for TiO_2 powders that were submitted to sonication treatment for 64 h or 32h and one with no treatment. Hysteresis loop was observed for all samples sonicated, suggesting that the structure of mesopores remained preserved.

Nitrogen adsorption isotherms of TiO_2 , sonicated for 64 h and calcined at 670 , 640 and 430°C and totally converted to rutile, are shown on Figure 7. Hysteresis loop is also observed here. The results obtained from rutile phase experiments are very important, because they indicate that the metastable anatase phase was converted to rutile with no collapse of mesopore structure.

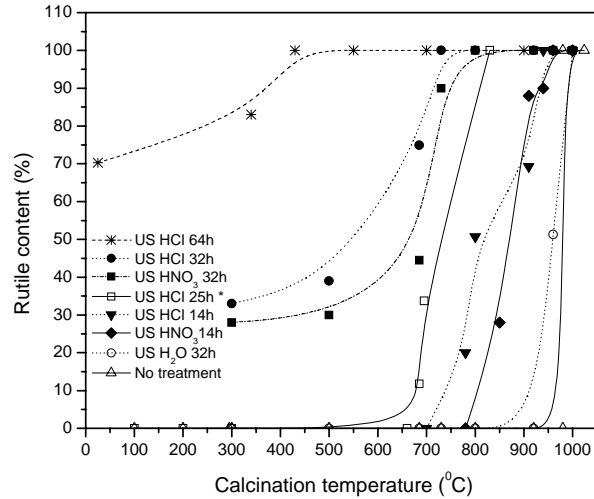


Figure 4: Rutile content vs. calcination temperature. 0, 14, 32 and 64 hours of sonication (US). Solvents: HNO_3 , HCl and water. Sulphate process (*).

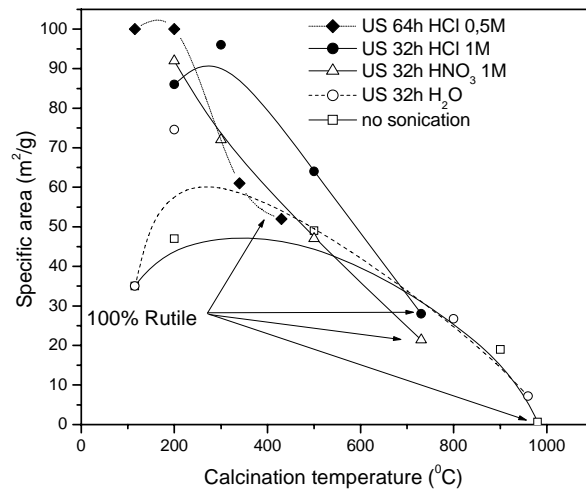


Figure 5: Variation of surface area with calcination temperature for hydrated TiO_2 (sample A) with and without sonication treatment (US).

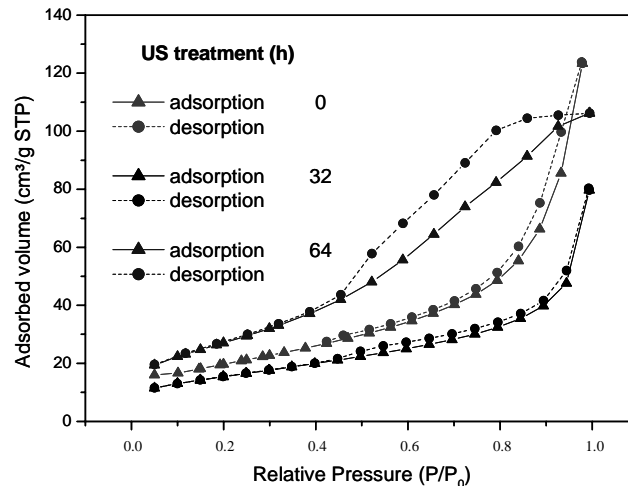


Figure 6: Adsorption isotherms of titania (sample A). Influence of period of sonication. No calcination was performed.

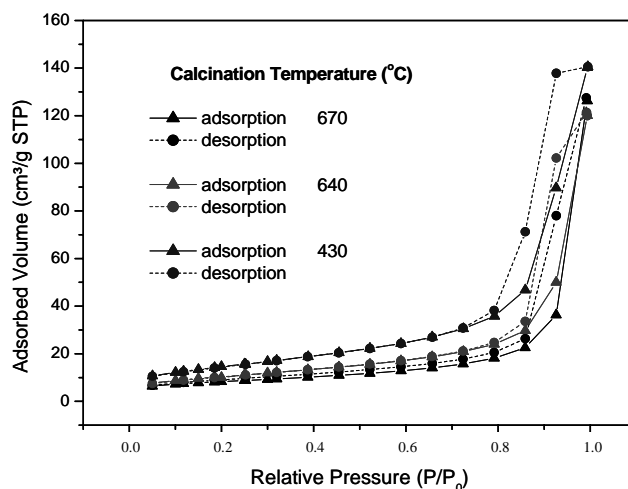


Figure 7: Adsorptions isotherms of titania (sample A) with US treatment.64 hours. Influence of calcination temperature. All the powders were in rutile phase.

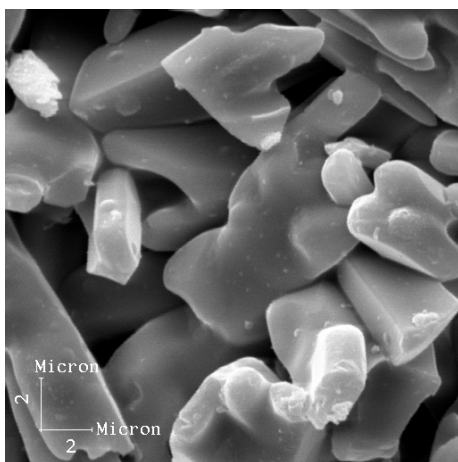


Figure 8: Powder micrograph. Calcination at 980°C. Rutile crystalline structure (x 3000).

A micrograph of TiO_2 powder calcined at 980°C for 3 hours is shown on Figure 8. Some prismatic crystals, grown simultaneously to the phase transition, are observed. The micrograph of Figure 9 shows the hydrated TiO_2 sonicated for 32 hours in 1M HCl and calcined at 730°C. The images of Figures 8 and 9 must be compared. Both of them were converted to rutile phase. However, Figure 9 shows a sample that was treated with ultrasound in acid medium. In this case, the rutile phase was obtained at 730°C while the sample of Figure 8 was obtained at 980°C. Rutile phase is in fact present in both samples. In spite of this, morphologic aspects, surface area and porosity are completely different, suggesting that this treatment is responsible for its transformation, as confirmed by BET surface area (28 m^2/g).

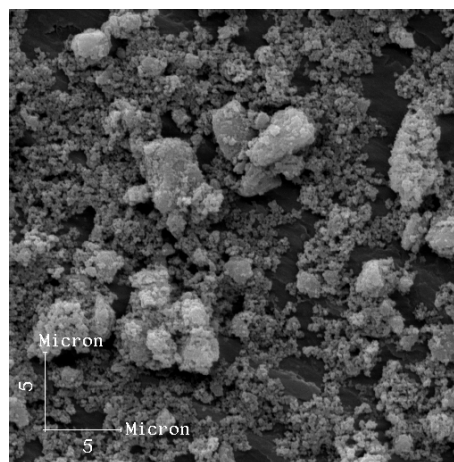


Figure 9: SEM. Sonicated powder (rutile) for 32 h, HCl 0.5M, calcination at 730°C. (x 3000).

Highly porous structures, with high concentration of defects, favor diffusion in the solid state, the most important mode by which transformation occurs during calcinations. Primary particle size derived from the sonication technique ranged between 13 – 18 nm, thus greater than those obtained by the sol-gel route, which yields particles suitable for fast transformations at 600°C (Yanagisawa and Ovenstone, 1999). Nevertheless, the high density of surface defects generated by sonication, in turn, plays a key role in increasing the kinetics and decreasing the transition temperature, in agreement with the work of Gribb and Banfield (1997).

The results of pre-treatment of titania particles with a high power ultrasonic field show the effects of sonication on the kinetics of anatase-rutile

transformation. The material with no treatment reached complete conversion to rutile around 1000°C (Figure 2), while materials submitted to sonication treatment for 14 h exhibited complete conversion to rutile around 900°C. Materials submitted to treatment for 32 h and calcined at 730°C were converted 100% to the rutile phase (Figure 4). Materials sonicated for 64 h, in turn, were partially converted to rutile phase at ambient temperature and reached complete conversion after calcination at 430°C and still kept surface area as high as 52m²/g (Figure 4 and 5).

Treatment with a sonorous field of high energy modified the texture of particles, surface morphology, and porosity, besides creating a high concentration of defects on the surface of particles. These effects favor the process of diffusion in the solid, which is the main mechanism involved in phase transformations in the solid state. The main goal when preparing catalytic oxides is obtaining a metastable material with as many defects as possible on its surface. The technique of sonication offers an alternative route to the production of crystals at low temperatures (without calcinations) and with high catalytic activity, as the formation of defects and preferential small sites is favored.

It was observed that titanium dioxide had its transition phase kinetics increased. Important practical consequence then result, as it allows transformation from anatase into rutile to be controlled, by varying the intensity of the treatment applied. This also enables preparation of TiO₂ for a number of other applications: membranes for processes of liquid separation and photocatalysts for organics degradation.

Adsorption isotherms type IV with hysteresis loop type H3, frequently found in processes involving pure solids with mesoporous structure such as inorganic and xerogel oxides, are similar to those shown in Figure 6-7, which represent the processes for TiO₂ sonicated for 64 h and converted to rutile at low temperatures. The volume of pores of the sonicated TiO₂ and rutile obtained at low temperatures was always larger than the original ones (amorphous or anatase). This favors the feasibility of a transition from metastable phase to steady state with no collapse of pore structure. On the other hand, TiO₂ in the rutile phase, obtained from calcinations at higher temperatures (without treatment with ultrasound), did not present isotherms with a clearly developed hysteresis loop, suggesting that a macroporous system may be predominant and no mesopore volume can be calculated (Greg and Sing, 1982 ; Sing, 1985).

Kumar et al. (1998) tried to stabilize the porous structure of titania by adding tin oxide particles to a pure titania matrix. Actually, tin oxide speeds up the anatase-rutile transformation by offering a similar crystallographic surface (crystalline structure of the SnO₂ is tetragonal as is rutile). This reduces the required surface energy for transformation; however, the best result obtained was to stabilize a porous structure with a specific surface of 16m²/g, for a conversion of 70% to rutile at 750°C. Conversion to 100% rutile was only reached at 800 °C and the specific surface in this condition was 8m²/g, representing almost total collapse of the porous structure. Kumar et al. referred to these results as a great success in stabilization of the structure of the pores of the titania. In this work, the biggest value of stabilization of the porous structure of titania 100% rutile phase was reached after sonication treatment for 64h in solution of 0.5M HCl and calcination at 430°C. In this situation rutile kept a high surface area of 52m²/g, indicating the importance of this result as a great scientific and technological contribution. Thus, ceramic membranes in the rutile phase could be used without collapse of the pore structure, while membranes of anatase used at high temperatures near that of the anatase-rutile transition.

Complete transformation into rutile, fast growth of grains and elimination of the porosity occur almost simultaneously. Near the transition, for materials whose transformations occur at high temperatures, particles reach remarkable growth and reduction of surface area is also considerable. The main reason for this drastic reduction of porosity and surface area is that primary particles inside a porous metastable system may grow or have density increased, or undergo both phenomena to reduce the demands of surface energy for formation of a new phase. During transformation of phase, atoms are very mobile because of rupture of links and an increase in sintering is expected near this temperature.

CONCLUSION

A new technique was conceived involving a pre-treatment by sonication prior to the stage of calcinations to speed up kinetics of anatase-rutile transformation. The process modified completely the texture of particles, morphology, and porosity, besides creating a high concentration of defects in the surface of particles. The technique showed that it is possible to obtain titania in the rutile phase at temperatures as low as 430°C, preserving elevated

surface area, suggesting thermal stability of the porous structure. The method offers an alternative route to reduce the phase transition temperature of metastable system by increasing the diffusion rate, probably due to creation of defects and increase of the density of active sites.

ACKNOWLEDGEMENTS

This work was supported by the Instituto de Engenharia Nuclear (IEN/CNEN) and the Universidade Federal do Rio de Janeiro PEQ/COPPE/UFRJ, Brazilian Federal Government Institutions.

REFERENCES

- Braun J. H., Titanium Dioxide – A Review, J. Coating Technology, Vol. 69 n. 868, May (1997).
- Cunha, J. W. S. D. and Silva, G. R. W., Processo para obtenção de óxido de titânio de alta pureza por extração líquido-líquido a partir do minério de anatásio, PI 0705592-7 (2007).
- Greg, S. J. and Sing, K. S. W., Adsorption, Surface and Porosity, Second Edition, Academic Press, (1982).
- Gribb, A. A. and Banfield, J. F., Particle size effects on transformation kinetics and phase stability in nanocrystalline TiO₂, American Mineralogist, 82, pp. 717-728 (1997).
- Kumar, K. N. P., Keizer, K. and Burggraaff, A. J., Pore-Structure Stability of Nanostructured Rutile Titania Containing a Structure Directing Second Phase Stabilizer, Materials Research Bulletin, Vol. 33 N/10, pp. 1495-1502 (1998).
- Sing, K. S. W., Everett, D. H., Haul, R. A. W., Pierotti, R. A., Rouquérol, J. and Siemieniewska, T. Reporting Physisorption Data for Gas/Solid Systems with Special Reference to Determination of Surface Area and Porosity, Pure Applied Chemistry, 57, pp. 603-619 (1985).
- Spurr, R. A. and Myers, H., Quantitative Analysis of Anatase-Rutile mixtures with an X-ray Diffractometer, Anal. Chem., Vol. 29, N 5, pp. 760-762 (1957).
- Yanagisawa, K. and Ovenstone, J., Crystallization of Anatase from Amorphous Titania Using the Hydrothermal Technique: Effects of Starting Material and Temperature, J. Phys. B (103), pp. 7781-7787 (1999).
- Yang, K., Zhu, J., Zhu, J., Huang, S., Zhu, X. and Ma, G., Sonochemical synthesis and microstructure investigation of rod-like nanocrystalline rutile titania, Materials Letters, 57, 30, December, pp. 4639-4642 (2003).
- Zhang, Y. H. and Reller, A., Investigation of mesoporous and microporous nanocrystalline silicon doped titania, Materials Letters, 57, pp.4108-4113 (2003).
- Zhang, Y. H. and Reller, A., Mesoporous Structure and Phase Transition of Nanocrystalline TiO₂, Materials Letters, 54 pp. 375-381 (2002).