

Thermal study of the anatase–rutile structural transitions in sol–gel synthesized titanium dioxide powders

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(Received 8 March, revised 30 August 2004)

Abstract: Titanium dioxide powders were synthesized by the sol–gel process using titanium tetrabutoxide as the precursor. The syntheses were performed in saturated aqueous solutions of KCl, CaCl₂, NiCl₂, CoCl₂ and MnCl₂, and in dimethylformamide (DMF) and dimethylsulfoxide (DMSO) solutions. The obtained X-ray diffraction patterns show that all samples were crystalline (anatase phase) with some minor amounts of a brookite phase. It is worth noting that the anatase phase was obtained independent of any previous or further treatment of the synthesized powder, such as hydrothermal or heat treatment. For the titanium dioxide powders synthesized in saturated aqueous solution of metal chlorides (mean crystallite size = 11 nm), the anatase–rutile transition occurred in the range 455–570 °C, depending on the considered sample, as verified by DTA analysis. In the powders synthesized in DMF or DMSO solutions (means crystallite size = 6 nm), the same structural transition occurred at 485 °C.

Keywords: sol–gel, anatase, titania, rutile.

INTRODUCTION

The sol–gel process¹ is one of the so-called “chemie douce”, routes. It has been widely employed as a synthetic route for the preparation of new materials,² providing very homogeneous samples, even at low synthesis temperatures.

It has been shown that, Ti–Zr nanocomposites with hexagonal structure³ and a series of Si–Al, Si–Ti, Si–Zr, Al–Zr, Al–Ti and Al–Ti–Zr⁴ nanocomposites with lamellar or hexagonal structure can be synthesized by the sol–gel process.

Titanium dioxide has been extensively studied because of its possible applications in various fields such as gas sensors, dielectric ceramics and photocatalyst,² and it has been shown that titanium oxide in the anatase phase can be synthesized at room temperature without any previous or further thermal or hydrothermal treat-

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ment by performing the hydrolysis and polycondensation processes in saturated metal chloride solutions.⁵

Titanium dioxide has three naturally occurring polymorphs, namely anatase, brookite and rutile.⁶ Despite criticisms of Liu and Merragh,⁷ rutile is considered to be the most stable polymorph at standard conditions. Anatase and brookite are considered to be kinetic products despite the fact that, depending on the particle size, anatase becomes more stable than rutile.⁸

It was shown that prior treatment of synthesized titanium oxide powders has remarkable effects on their properties, as well as on the structural transitions observed under heating.^{9,10} The anatase–rutile transition is exothermic and irreversible, occurring in the range 400–1200 °C.^{9,10}

The aim of this publication is to report on a thermal study of the anatase–rutile structural transition of anatase powders obtained by the sol–gel process. The titanium dioxide syntheses were performed in saturated aqueous solutions of metal chlorides, as well as in dimethylformamide (DMF) and dimethylsulfoxide (DMSO) solutions.

EXPERIMENTAL

The titanium oxide powders were obtained by the hydrolysis and polycondensation of titanium tetrabutoxide (Aldrich) in water and aqueous saturated solutions of KCl, CaCl₂, NiCl₂, CoCl₂ and MnCl₂, as previously mentioned.⁵ In a typical synthesis, 5 cm³ of titanium butoxide were added to 50 cm³ of a saturated solution of a metal chloride at 25 °C, and the resulting mixture was stirred for 30 s. The obtained powders were aged for 24 h and then washed several times with deionized water and dried under vacuum at room temperature for 20 h.

Hydrolysis and polycondensation of titanium tetrabutoxide were also performed in dimethylformamide (DMF) and dimethylsulfoxide (DMSO). In a typical synthesis, 5 cm³ of titanium tetrabutoxide were added to 50 cm³ of DMF or DMSO, under stirring. The obtained solutions were aged for 48 h, and then, 1.5 cm³ of deionized water was added. The obtained powders were aged for 24 h and then washed several times with deionized water and dried under vacuum at room temperature (25 °C) for 24 h.

The X-ray diffraction patterns were recorded on a Shimadzu apparatus using Cu-K α radiation. The TG–DTA curves were obtained under an argon atmosphere at a heating rate of 10 °C min⁻¹, using a DuPont instrument.

RESULTS AND DISCUSSION

All the titanium dioxide powders synthesized in saturated aqueous solutions of metal chlorides were crystalline. The mean crystallite size was calculated from the broadening of the $2\theta = 25^\circ$ peak of the (101) diffraction plane, ($d = 0.36$ nm) and found to be 11 nm for all samples. The titanium dioxide powders synthesized in DMF or DMSO solutions were also crystalline. From the peak broadening of the anatase (101) diffraction, the mean crystallite sizes were calculated to be 6 nm for both samples. Hence, it can be verified that the mean crystallite sizes are strongly affected by the composition of the reaction media and that organic species induce the formation of crystallites of smaller dimensions.

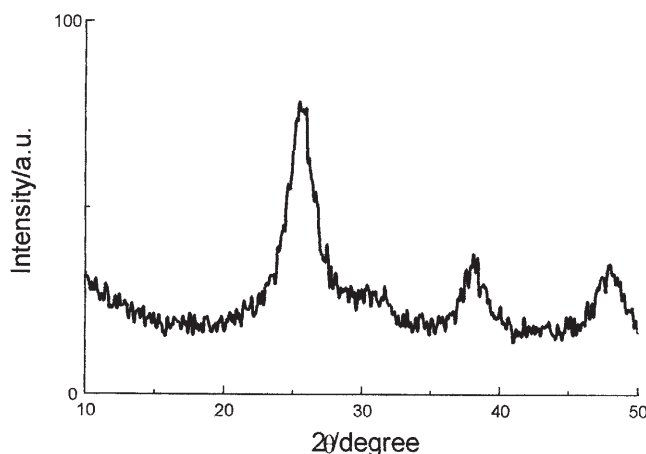


Fig. 1. X-Ray diffraction pattern of a titanium dioxide powder obtained by the sol-gel process in DMF.

It is worth noting that all the synthesized titanium dioxide samples were crystalline as synthesized, with no necessity of any previous or further treatment, such as heating or hydrothermal aging, as was observed for other sol-gel derived titanium dioxide powders.^{9,10} This phenomenon is probably related to the formation of OTi_3 groups, which could favour the formation of the anatase phase, having a localized structure with four edges shared by TiO_6 octahedral units, instead an amorphous phase, with only two shared edges.¹⁰⁻¹³

The X-ray diffraction patterns of all diffraction peaks, including the one around $2\theta = 25^\circ$, confirm that anatase is the formed crystalline phase.^{9,10} On the other hand, the diffraction peak around 30° could be attributed to the presence of a minor amount of the brookite phase.^{9,10} Obviously, the presence of organic molecules (DMF or DMSO) or metal chloride ions provides new paths for the hydrolysis and polycondensation processes which lead to ordered matrices, instead of amorphous ones as was observed if the hydrolysis and polycondensation processes are performed in water. The X-ray diffraction pattern for titanium dioxide powder synthesized in DMF is shown in Fig. 1, as an illustrative example.

The anatase-rutile structural transition, of the titanium dioxide powder synthesized in CaCl_2 solution, occurred at 512°C , as was verified by the well defined exothermic peak. This transition occurred at $460, 455, 510$ and 570°C for the titania powders synthesized in K, Ni, Co and Mn chlorides solutions, respectively. Thus, variations of 55°C can be observed for this structural transition, depending on the metal chloride employed.

In the DTA curves of DMF or DMSO synthesized titanium dioxide samples, an endothermic peak from $30-250^\circ\text{C}$ was observed, which was associated with a significant mass loss step (TG curves), attributable to the removal of physisorbed water and DMF or DMSO molecules, as well as of unreacted titanium alkoxide.

The anatase-rutile structural transition, associated with a well-defined exothermic peak, occurred at 485°C for both samples. Such a fact suggests that the

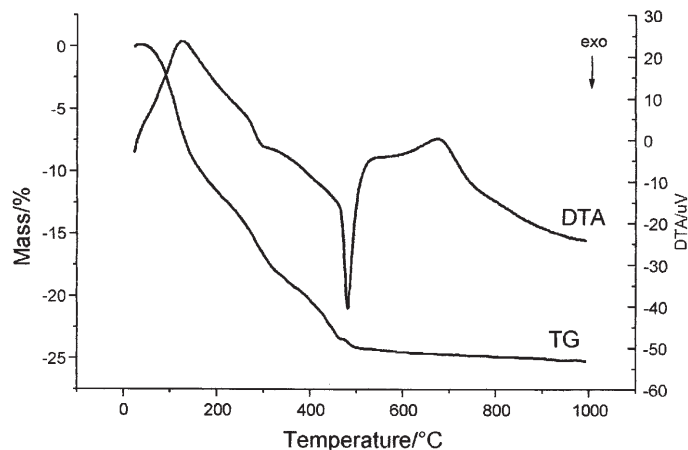


Fig. 2. TG-DTA Curves for a titanium dioxide powder obtained by the sol-gel process in DMF.

temperature of the structural transition is associated with the mean crystallite size, which was the same, for both samples. An endothermic peak was observed from 600 °C to 800 °C for both samples, which was associated with a minor mass loss step, probably due to the sublimation of a minor amount of powder or the thermal degradation of the last alkoxide molecules, trapped in the three-dimensional network oxide structure. The TG-DTA curves for the DMF synthesized powder is shown in Fig. 2 as an illustrative example.

The formation of a rutile phase in amorphous and hydrothermally treated titanium dioxide powders was observed to start in the range 700–820 °C.⁹ Hence, the titanium dioxide powders synthesized in this work allow the formation of a rutile phase at temperatures about 200 °C below this temperature range. Such a fact is probably related to the mean crystallite size, which are smaller for the samples prepared in this work.

CONCLUSION

The obtained experimental results show that organic species (DMF and DMSO, in this case) induced the formation of titanium dioxide crystallites of small dimensions (6 nm). Furthermore, the temperatures needed to promote the anatase-rutile structural transition can be reduced by 200 °C, if compared with another sol-gel prepared titanium dioxide powders,⁹ by using the experimental procedures reported in this work.

ИЗВОД

ТЕРМИЧКА ПРОУЧАВАЊА СТРУКТУРНОГ ПРЕЛАЗА АНАТАЗ–РУТИЛ
КОД СОЛ–ГЕЛ СИНТЕТИСаниХ ПРАХОВА ТИТАНИЈУМ–ДИОКСИДАROBSON F. DE FARIAS^{*1}, CECILIA C. GUEDES E SILVA² and THOMAZ A. G. RESTIVO²

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Прахови титанијум-диоксида синтетисани су сол–гел поступком коришћењем титанијум тетрабутоксида као прекурсора. Синтезе су извођене у засићеним воденим растворима KCl, CaCl₂, NiCl₂, CoCl₂ и MnCl₂, као и у растворима у диметилформамиду (DMF) и диметилсулфоксиду (DMSO). Добијени дифрактограми показују да су узорци кристалични (анатаз фаза) уз мале количине брукит фаза. Треба назначити да је анатаз фаза добијана независно од ма ког претходног или накнадног третирања синтетисаног праха, хидротермалног или топлотног. Код титанијум-диоксидних прахова синтетисаних у засићеним воденим растворима хлорида метала (средње величине кристалита = 11 nm) прелаз анатаз–рутил одигравао се у температуром опсегу 455 – 570 °C, у зависности од посматране врсте, као што је показала DTA анализа. Код прахова синтетисаних у DMF или DMSO (средње величина кристалита = 6 nm) овај структурни прелаз одигравао се на 485 °C.

(Примљено 8. марта, ревидирано 30. августа 2004)

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