

A NEW EXPERIMENTAL PROCEDURE TO OBTAIN TITANIA POWDERS AS ANATASE PHASE BY A SOL-GEL PROCESS

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Titania powders were synthesized by a sol-gel process using titanium tetrabutoxide as precursor. The syntheses were performed in water or in solutions of dimethylformamide (dmf) or dimethylsulfoxide (dmsO). It is demonstrated, by X-ray diffraction patterns of the synthesized powders, that the samples obtained in dmf or dmsO solutions are crystalline (anatase phase) with some minor amount of brookite phase, whereas the sample synthesized in water is amorphous. The anatase phase can be obtained independently of any previous or further treatment of the synthesized powder, such as hydrothermal or heat treatment, providing a new, simple, quick and inexpensive route to synthesize anatase powders. From the peak broadening of the anatase (101) diffraction, the crystallite sizes were calculated as 6 nm.

Keywords: titania; anatase; sol-gel; X-ray diffraction.

INTRODUCTION

Taking into account its possible applications as gas sensor, dielectric ceramic or photocatalyst¹, titanium dioxide, TiO₂, has been extensively studied. The sol-gel process² has been employed as a successful synthetic approach to obtain titania³ or titania-zirconia⁴ powders with spherical morphology.

Titania has three naturally occurring polymorphs named anatase, brookite and rutile⁵. Rutile has been considered the most stable polymorph at standard conditions. Anatase and brookite are considered as kinetic products. On the other hand, depending on the particle size, anatase becomes more stable than rutile⁶.

Many investigations dealing with the structural transitions of sol-gel synthesized titania powders have been performed, and it has been shown that hydrothermal and heat treatment of amorphous titania^{7,8} can exert remarkable influences on the structural transitions.

In such kind of investigations, it has been demonstrated that the sol-gel synthesized titania powders are always amorphous in nature, and that a crystalline structure is achieved only after a heat treatment, at a temperature dependent on the temperature of a previous hydrothermal treatment^{7,8}.

The purpose of this publication is to demonstrate that titania powders obtained by a sol-gel process performed in dimethylformamide (dmf) or dimethylsulfoxide (dmsO) solutions are crystalline (anatase phase), independent of any further or previous hydrothermal or heat treatment, providing a new, simple, quick and inexpensive route to synthesize anatase powders.

Dimethylformamide and dimethylsulfoxide were chosen taking into account their nucleophilic nature, which could exert kinetic effects on the titanium alkoxide hydrolysis.

EXPERIMENTAL

Hydrolysis and polycondensation of titanium tetrabutoxide (Aldrich) were performed in water and solutions of dimethylformamide (dmf) or dimethylsulfoxide (dmsO). In a typical

synthesis, 5 cm³ of titanium tetrabutoxide was added to 50 cm³ of water, dmf or dmsO, under stirring. For dmf and dmsO systems, 1.5 cm³ of deionized water was added to the solution. The powders were aged for 24h, and then exhaustively washed with deionized water and dried under vacuum at room temperature for 48 h. Infrared spectra indicate that no organic moiety is present in the powders, after the washing operation.

The X-ray diffraction patterns were recorded with a Shimadzu apparatus using Cu-K α radiation.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of the synthesized samples are shown in Figure 1. As can be observed, titania powders synthesized in dmf or dmsO solutions are crystalline, whereas the sample synthesized in water is amorphous. It is worth noting that the samples are crystalline as synthesized, without needing any previous or further treatment such as heating or hydrothermal aging, as observed for other sol-gel derived titania powders^{7,8}. This phenomenon is probably related with the formation of TiO₃ groups, which could favour the formation of the anatase phase, with a localized structure with four edges shared by TiO₆ octahedral units, rather than the amorphous phase, with only two shared edges⁹⁻¹².

All peaks, including that one around 25°, confirm that anatase is the crystalline phase formed^{7,8}. On the other hand, the diffraction peak around 30° can be attributed to the presence of a minor amount of brookite phase^{7,8}. Obviously, the presence of the organic molecules (dmf or dmsO) provides new paths for the hydrolysis and polycondensation processes, leading to ordered matrices, instead of amorphous ones. From the peak broadening of the anatase (101) diffraction, the mean crystallite sizes were calculated as 6 nm (Scherrer's equation).

CONCLUSION

Since the powders synthesized in dmf or dmsO are crystalline in nature independent of any previous or further treatment of the synthesized powder, such as hydrothermal or heat treatment, the experimental procedure proposed is a new, simple, quick and

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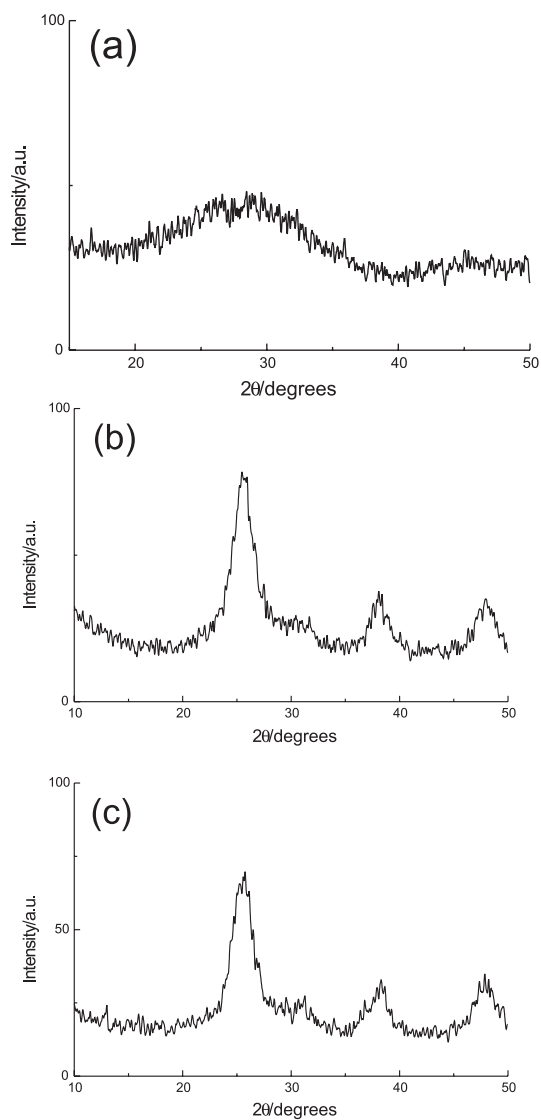


Figure 1. X-ray diffraction patterns for titania powders obtained by a sol-gel process in water (a), dmf (b) and dmsol (c)

inexpensive route to synthesize anatase powders. As can be observed, by comparing the X-ray diffraction patterns of the synthesized matrices, anatase is always the crystalline phase obtained, independent on the specific solvent used (dmf or dmsol).

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