

Production Of Nanoparticles Of Titanium Dioxide By Using A Spinning Disc Reactor

M. Stoller^{a*}, M. Mescia^b, C. Valencia Peroni^b, A. Chianese^a

^a Department of Chemical Engineering, Sapienza University of Rome

Via Eudossiana 18, 00184 Rome, Italy

^b LABOR s.r.l.

Via G. Peroni 386, 00131 Rome, Italy

* Corresponding author: stoller@ingchim.ing.uniroma1.it

This explorative work deals with an experimental investigation concerning the production of titanium dioxide as nanoparticles and sol-gel material, by using a spinning disc reactor. The obtained results are compared with those obtained by using a traditional stirred tank reactor. Titanium dioxide particles down to ten nanometres in size were produced. The sol-gel material was used for coatings glass slides with titanium dioxide layers tenths nanometres in thickness. The contact angle technique was adopted to evaluate the coated surface hydrophobicity.

For both the investigated titanium dioxide synthesis, the spinning disc reactor permits to produce particles and coatings of higher quality, if compared to the results obtained by using the stirred tank reactor.

Introduction

There is an increasing demand for titanium dioxide of controlled quality for many applications: cosmetics, heterogeneous photocatalysis and surface coating.

There are many methods to produce TiO₂ nanopowders such as the chemical vapour deposition (J.A. Agillon et al., 1999), the oxidation of titanium tetrachloride (M.K. Akhtar et al., 1991; H.D. Jang, 1997) and flame synthesis (Wooldridge M.S., 1998; Pratsinis S.E., 1998).

Nowadays, the most used method to industrially produce nanopowders of titanium dioxide is based on plasma spray synthesis (PSS) technique. This method allows a high productivity, but leads to the production of nanoparticles containing impurities which reduce the quality grade of the product. Moreover, the control of crystal's phase, shape and size distribution of the produced nanoparticles is not straight forward as it depends strongly from the of the spray feedstock (Zhanga T., 2006). On the contrary, production of nanoparticles by chemical precipitation is the best method to assure a high purity degree of the final product. In particular, precipitation may give rise to sol-gel material to be used for different coating applications in catalyst production, autocleaning glass, antireflection film, etc.

The main drawback of the precipitation process is the difficulty to control the crystal size distribution. A very important factor to achieve this target is to attain a high local mixing, that is micromixing, between the reagents in the used reactor apparatus in order

to have a homogeneous nucleation and a narrow distribution of the produced nanoparticles. A lab apparatus, known as T-mixers, can realize the needed micro mixing (Stoller and Chianese, 2006), but with a huge specific energy dispersion, unsuitable for industrial application. Baffi et al. (2002) showed that comparable results may be achieved by using a rotating spinning disc reactor (SDR) but at a reasonable energy consumption, therefore this latter technique appears to be the unique one to obtain micromixing conditions at industrial scale.

This explorative work deals with an experimental investigation concerning the production of both titanium dioxide nanoparticles and titanium dioxide sol-gel material, by using a spinning disc reactor. The obtained results are compared with those obtained by using a traditional stirred tank reactor (STR). The two examined processes to produce nanoparticles and sol-gel material, respectively, are reported in this paper in two separate sections.

PART I: Production of nanoparticles

Experimental setup

The titanium dioxide nanoparticles were produced by hydrolysis of titanium tetraisopropoxide (TTIP). TTIP $[\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4]$ supplied by Sigma-Aldrich with a purity of 97% was used without any further purification. Two different precipitation reactors were used. The first apparatus is a stirred tank vessel, 100 ml in capacity, provided with a magnetic stirrer and a thermostatic jacket. The experimental procedure was as follows: TTIP was initially charged in the vessel, then a stream of distilled water was fed at a constant flow rate to induce precipitation.

The second apparatus was a rotating spinning disc reactor, reported in Fig. 1. The disc, made by brass is 300 mm in diameter and may rotate at a speed up to 1500 rpm. In this case there was the contemporary feeding of the reagent solutions over the disc. The injection points were placed at the same distance from the radial centre of the system, equal to 10 cm, thus at 180° each other. Both the apparatuses were operated at a temperature of 25°C , at a ratio distilled water-TTIP equal to 2/15 and in presence of a small amount of nitric acid.

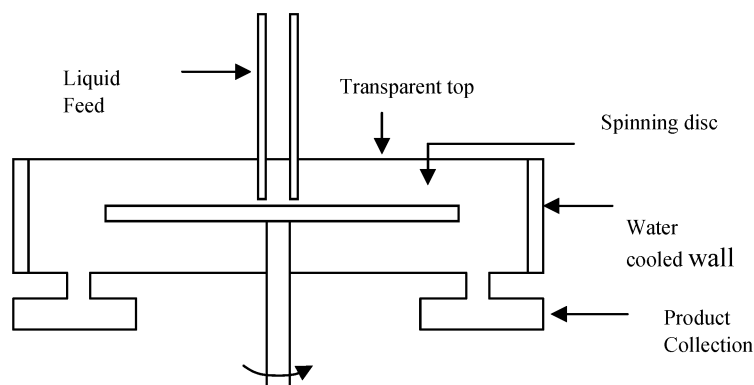
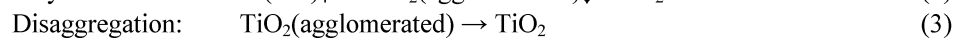
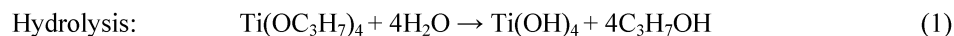


Figure 1: Scheme of the SDR.

The reaction leads to titanium dioxide which precipitates quickly from the solution since this metal oxide is slightly soluble in water. The reaction system consists of the following reactions (Hintz et al., 2004):



The precipitated nanoparticles were highly agglomerated and exhibited a relatively high dimension up to a few millimetres. After the precipitation step, the particles suspension was maintained in a stirred vessel at 1000 rpm for 24 hours in order to promote the redispersion of agglomerates due to the action of nitric acid. At fixed interval of time the polydisperse particle size distribution of titania was measured by means of a dynamic light scattering instrument.

The nanoparticles were separated from the solution by a freeze drying operation.

Results and Discussion

The efficiency of the two apparatuses for the production of TiO_2 nanoparticles was evaluated on the basis of the size distribution of the solid produced after 24 hours of stirring in presence of nitric acid 0.1 M. Figure 2 shows the size distributions by intensity of the two nanoparticles population after 24h of redispersion time.

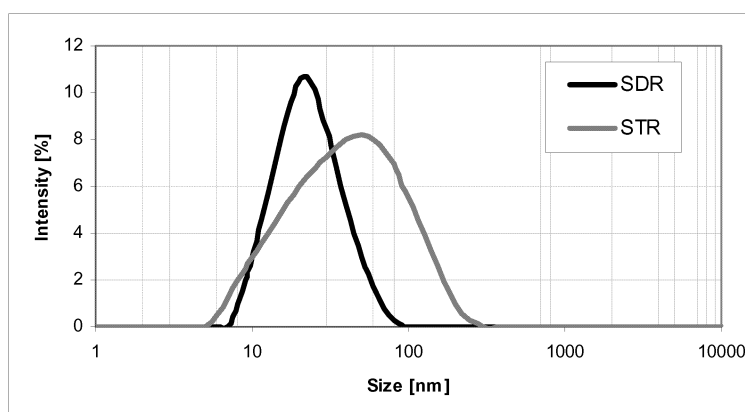


Figure 2: Size distribution of TiO_2 nanoparticles in presence of nitric acid 0.1 M

The nanoparticles produced by using the SDR exhibits a monomodal and narrow size distribution, in the range 7–90 nm, with an average size of 24 nm, whereas the nanoparticles obtained by adopting the STR exhibit a relatively wide and asymmetric particle size distribution, in the range 5–300 nm, and a higher average size, around 50 nm. Thus, by applying the same recipe, the better hydrodynamic conditions attained in the SDR unable to produce a better nanoparticles distribution, quite narrow, with a smaller average size. The best performances obtained by the SDR were possibly due to

the occurring of micro mixing over the disc surface, which cannot take place in the STR. In all the runs the solid phase of the produced particles was essentially anatase. It is interesting to examine the evolution of the size distribution along the redispersion time, reported in fig. 3. The samples were prepared by means of the STR with two different nitric acid concentrations, that is 0.4M and 0.625M, and a subsequent redispersion for 24h at a stirring rate of 200rpm.

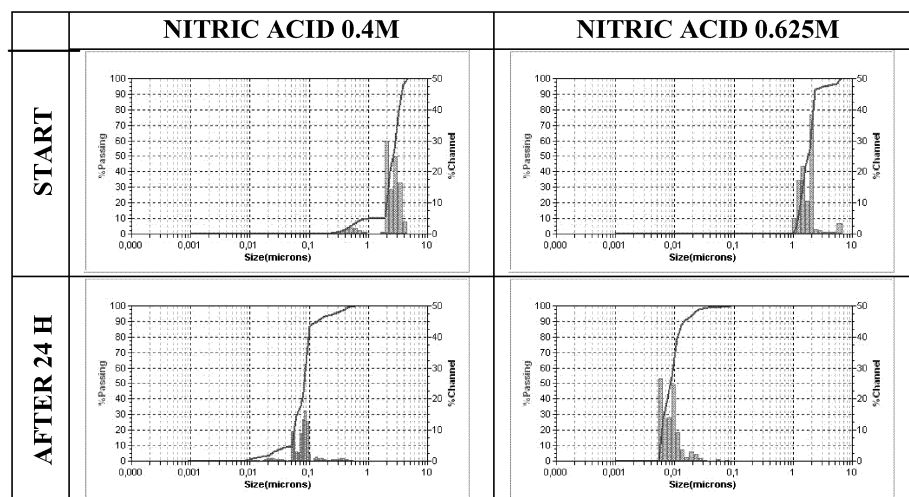


Figure 3: Size distribution changes as function of the redispersion time.

The particles size up to 5 millimetres at the run start, is strongly reduced after 24 h of redispersion time but only in the case of nitric acid 0.625 M only nanoparticles are obtained. Therefore, the effectiveness of the disaggregation is a function of time and nitric acid concentration, as expected.

Part II: Production of titania sol-gel material

Experimental set-up

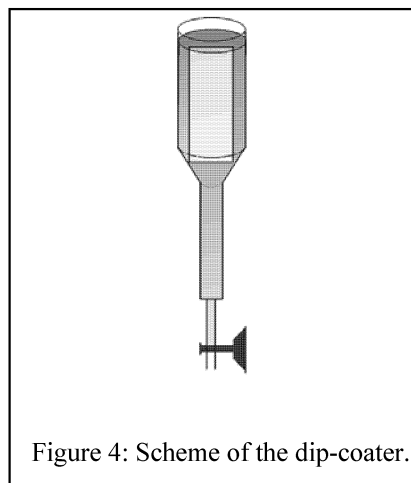


Figure 4: Scheme of the dip-coater.

For the production of the titanium dioxide sol-gel material a solution of isopropanol and TTIP was put in contact with a solution of isopropanol and hydrochloric acid. Both the reactor apparatuses, i.e. SDR and STR, were still used. The reagents were separately fed by using the SDR, whereas, when the STR was adopted, initially the solution of isopropanol and hydrochloric acid was charged in the vessel, then the isopropanol solution with TTIP was fed at a constant flow rate drop wise. An overall constant ratio between TTIP and isopropanol was always assumed, equal to 1/5.

Afterwards, the sol-gel material was withdrawn from the reactor apparatus and poured in the coating vessel.

The produced sol-gel material was used to cover glass surfaces (microscopy glass slides, dimension 75x25x1) by means of a dip coating process. For this purpose the glass slide was put in a home made deep coater, shown in fig. 4: the air in the vessel was replaced by dried nitrogen and the sol gel material was then carefully poured into the coater. The coating was undertaken by very slow discharge rate of the sol gel material from the bottom of the coater. The discharge period of time was between 20 and 30 minutes. The coated glass still remained inside the coater for some more tenths of minutes to start the dryness in a dry atmosphere.

Finally, the quality of the coating layer was evaluated on the basis of the hydrophobicity of the surface of the glass slide. For this purpose, the contact angle of a distilled water drop over the slide surface was measured in presence or not of an UV light.

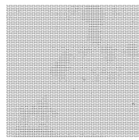
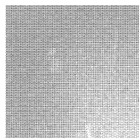
Results and Discussion

The adopted reaction system gives rise to a sol-gel process, where nanometric colloidal particles (sol) or macropolymer structure (gel) may be produced according to the applied operating conditions. In particular, after the first two reactions of hydrolysis and condensation (see eq. 1 and 2), oxopolymer sol nanoparticles with a general formula $TiO_a(OH)_b(OR)_{4-2a-b}$ are produced (Rivallin et al., 2005). The third reaction of the sol-gel process is as follows:



It induces the gel network: the colloidal solution loses its stability and a macroprecipitation occurs. As shown by Rivallin et al. (2005) the aggregation of sols occurs in a relatively long period of time, up to some tenths of minutes, called also “induction time”. The induction time is accelerated by the presence of water, if it is present in solution. The coating operation can be performed during the induction time and is as much uniform as more homogeneous is the sol distribution in the sol-gel material.

Table 2: Results obtained by glass coating by using sol-gel material produced by STR and SDR, respectively.

OPERATING CONDITIONS	SDR	STR
ROTATING OR STIRRING SPEED, rpm	1440	1500
CONTACT ANGLE IN ABSENCE OF UV RADIATION, °	83	65
CONTACT ANGLE IN PRESENCE OF UV RADIATION, °	58	43
IMAGE OF THE COATED LAYER UNDER AN OPTICAL MICROSCOPE		

By optimising both the reaction and coating procedure, it was possible to produce nanoparticles layers a few tenths of nanometres in size. First of all, a comparison was made between two coated glass surfaces by using a sol-gel material produced by the SDR and the STR (see Table 2). A smoother and homogeneous surface as well as higher contact angles were obtained when SDR was adopted, thus confirming the production of a more homogeneous material when the SDR is used.

The UV light get more hydrophilic the coated surface, as expected. The difference between the two contact angles indicates the photoactivity of the produced coated layer.

Conclusions

The spinning disc, applied to the precipitation of TiO_2 , appears to be a worthwhile technique to produce uniform nanoparticles even as sol in a sol-gel material. When nanoparticles are produced by precipitation from sol-gel the overall process consists of two stages: firstly the precipitation of nanostructured nanoparticles are produced, then a subsequent disaggregation stage by using nitric acid give rise to smaller aggregated particles depending on the pH and run time. However, by applying the same operating conditions SDR provide more uniform and smaller nanoparticles with respect to STR. The production of more uniform sol in sol-gel material is also obtained by SDR than by STR. In fact, the coating of glass slide performed by sol-gel produced by SDR allow a very smooth and homogeneous coating layer, a few tenth nanometres in size.

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