Eurasian ChemTech Journal 10 (2008) 19-23

Synthesis and Characterization of Thermally Stable Mesoporous Titania

Ch. Subrahmanyam*, S. Shanmugam, B. Viswanathan and T.K. Varadarajan

Department of Chemistry, Indian Institute of Technology-Madras, Chennai-600 036, India

Abstract

A new synthetic approach was followed for the preparation of mesoporous titania, where polyethylene glycol-400, a water soluble polymer was employed as hydrolysis retarding agent. Mesoporous titania was characterized by low angle XRD, N_2 adsorption, transmission electron microscope and thermal analysis, which confirm the formation of mesophase and also the thermal stability of the prepared material.

Introduction

With the discovery of mesoporous solids by Mobil researchers, many attempts have been made to synthesize various non-siliceous oxides in mesoform [1]. Majority of the synthetic routes for the production of non-siliceous mesoporous oxides involve either the use of organic species, which will form liquid crystals, or the amphiphilic block copolymers as structure directing agents. A co-operative templating mechanism has been speculated in all these cases that is sensitive to synthetic parameters like surfactant concentration, aging time and also hydrothermal synthesis conditions. Among the non-siliceous mesoporous oxides, special attention has been paid mainly to the synthesis of titania in mesoporous form.

A report on the synthesis of mesoporous titania appeared in 1995 by a modified sol-gel route with phosphate surfactants that combined the principles of liquid crystal templating and the sol-gel procedure [2]. In this procedure, it was observed that acetylacetone was required to delay the condensation process of the titanium precursor. Even though as-synthesized materials show well-ordered hexagonal structures, calcination of these materials yielded solids with low BET surface area values (~200 m^2/g). Like wise, a few attempts have also been made to prepare thermally stable titania where anionic [3,4] and cationic surfactants were used [5]. In a similar approach, neutral surfactants have also been tried to prepare mesoporous titania. However, in all these methods, either removal of surfactant caused structural collapse or the final material has a BET surface area that was less than 100 m^2/g.

On careful observation it can be found that synthesis of mesoporous titania is governed by the controlled precipitation of titanium precursor, specific temperature for the synthesis and the easy removal of the surfactant. By achieving an adequate balance between the rate of hydrolysis and condensation process, it is possible to synthesize thermally stable mesoporous titania. Due to faster rate of hydrolysis of the titanium precursor, there is a need to optimize the hydrolysis rate so as to achieve a stable homogeneous gel. In this connection, Antonelli used acetylacetone in acidic medium to obtain a stable gel [4]. The use of anionic surfactant dodecylphosphate was also reported where pH was maintained in the range 4-6 with dilute HCl [6]. Among the other known complexing agents, water-soluble triethanolamine was used to control the hydrolysis rate [5]. However, water soluble polymers with lower molecular weights can also serve this purpose, especially polyethylene glycol, with low molecular weights, which can be easily removed by simple calcination under mild conditions (250-400°C) depending on the matrix in which it is present. In the present study, polyethelene glycol (PEG 400) was used as hydrolysis retarding agent. This is due to its miscibility with

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*corresponding authors. E-mail: csubbu@nitt.edu

Printed in Kazakhstan

Ti-precursors. In the present study, thermally stable mesoporous titania was prepared by using cetyltrimethylammonium bromide (CTAB) as template and tetrabutylorthotitanate as titanium precursor.

Experimental

Synthesis of Mesoporous Titania

The synthesis is based on the use of a cationic surfactant (CTAB) as a structural directing agent and a complexing agent polyethylene glycol (PEG-400) as hydrolysis retarding agent. In the typical synthesis 0.0066 mole of CTAB was dissolved in 60 ml of water. Then a solution containing 0.0198 mole of titanium n-butoxide and 0.0066 mole of polyethylene glycol was added to CTAB solution slowly by maintaining pH around 10.5 with tetramethylammonium hydroxide .The solution was stirred for three hours in nitrogen atmosphere. Then it was loaded in a stainless steel autoclave and hydrothermally treated at 423 K for 24 hrs. The mixture was filtered and washed with ethanol + water mixture and oven dried. Calcination was carried out at 823 K in N_2 atmosphere for 2 hrs followed by air for 5 more hours [7]. For the synthesis of mesoporous TiO_2 in the present study, TMAOH was used as base source to maintain pH around 10.5 as other sources resulted in amorphous materials. This may be due to high rate of hydrolysis of Ti-alkoxides in the presence of strong base.

When the synthesis was carried out with out any modification of the reported procedures, only amorphous materials resulted. This was due to the rapid hydrolysis of Ti-precursor. Moreover, when the synthesis was carried out only in polymer (PEG-400), then also it resulted in amorphous material, which rules out the possibility preparing the material with simple polymers like PEG-400. These results indicate that there should be an optimum concentration of the polymer with respect to inorganic precursor. As mentioned earlier, by achieving an adequate balance between hydrolysis and condensation process it is possible to produce mesoporous TiO_2.

Though, syntheses of inorganic solids especially, mesoporous solids were reported with polymeric surfactants, there has been no report on the formation of such network with the complexing agent used in the present study *i.e.* PEG-400 [8]. This is due to the fact that PEG-400 cannot form micellar arrangement in water medium. For the formation of the micelles in solution, there should be different moieties with hydrophilic/hydrophobic difference.

Characterization

The X-ray diffraction (XRD) patterns were recorded on D500 Siemens powder diffractometer (θ/2θ) using monochromatized Cu K_α radiation (λ = 1.5406 Å) in the 2θ range of 0.5-10° in the steps of 0.04° and a step time of 8 s. Surface area measurements were done by the adsorption-desorption of N_2 at 77 K using Sorptomatic 1990 (Carlo Erba) instrument. Samples before the measurements were out gassed for 12 hrs to remove the physi-sorbed gases. The specific surface area values (SSA) of the samples were calculated employing the BET equation, while BJH method was used to calculate pore-size distribution. HRTEM measurements were carried out on Philips CM300UT FEG with 300 kV field emission gun, whereas thermal analyses of the samples were made with thermal analyzer (PerkinElmer model TGA 7) at a heating rate of 20 K/min.

Results and Discussion

XRD

XRD patterns of the uncalcined and calcined mesoporous titania are shown in Fig. 1a, b and c. As-synthesized material shows XRD pattern with a maximum intense peak in addition to less resolved peaks. The observed pattern can be indexed to d_{100}, d_{110} and d_{200} reflections of a hexagonal unit cell, which is characteristic of mesoporous solids [1]. As-synthesized material shows a d_{100} spacing of 3.35 nm, which upon calcination decreases to 3.20 nm indicating less long-range crystallographic order. pH of the synthesis gel was adjusted to 10.5 with tetramethylammonium hydroxide. As stated earlier, when NaOH or NH_4OH was used as a base instead of tetramethylammonium hydroxide, only amorphous material was obtained. This clearly indicates the need to maintain the pH of the synthesis gel with a milder base like TMAOH. The function of the organic ammonium cation of TMAOH is probably to modify the strength of the electrostatic interactions between the inorganic precursor species and the cationic surfactant micelle assembly to form a stable gel. If either NaOH or NH_4OH is used, the smaller cations Na^+, NH_4^+ compete with the TiO^-

species and thus restrict the interaction with the positively charged cationic surfactant. However, it can be seen from the XRD pattern of the calcined material that the higher order reflections are absent. However, the d_{100}peak is still retained and this peak is shifted slightly to higher d-value confirming the partial disorder of titania after calcination. It has been observed that the titania prepared in this procedure exhibits thermal stability up to 973 K unlike the materials reported in the literature where, upon the removal of the surfactant the ordered structure collapses and becomes non porous. The high thermal stability of the mesoporous titania might be due to the formation of stable homogeneous gel that facilitates sufficient condensation process. To examine the thermal stability of the mesoporous titania, as-synthesized material has been calcined at various temperatures in order to remove the surfactant. Figures 1c represents the X-ray diffractograms of the mesoporous titania calcined at 973 K. It can be seen that the mesoporous titania is stable up to 973 K. The material calcined at 973 K shows low angle diffraction peaks indicating that the mesoscopic order has been preserved in the sample.

For titania prepared at higher concentrations of polyethylene glycol (PEG/Ti > 0.3), XRD is not well resolved. These materials are not thermally stable like the material prepared with (PEG/Ti ~ 0.3-0.4). This may be due to the difficulty in the removal of PEG at higher concentrations. During the removal of surfactant by calcination process, the excess of heat generated because of exothermic process (combustion of carbon) may lead to the collapse of the mesostructure and impart less thermal stability to the final material.

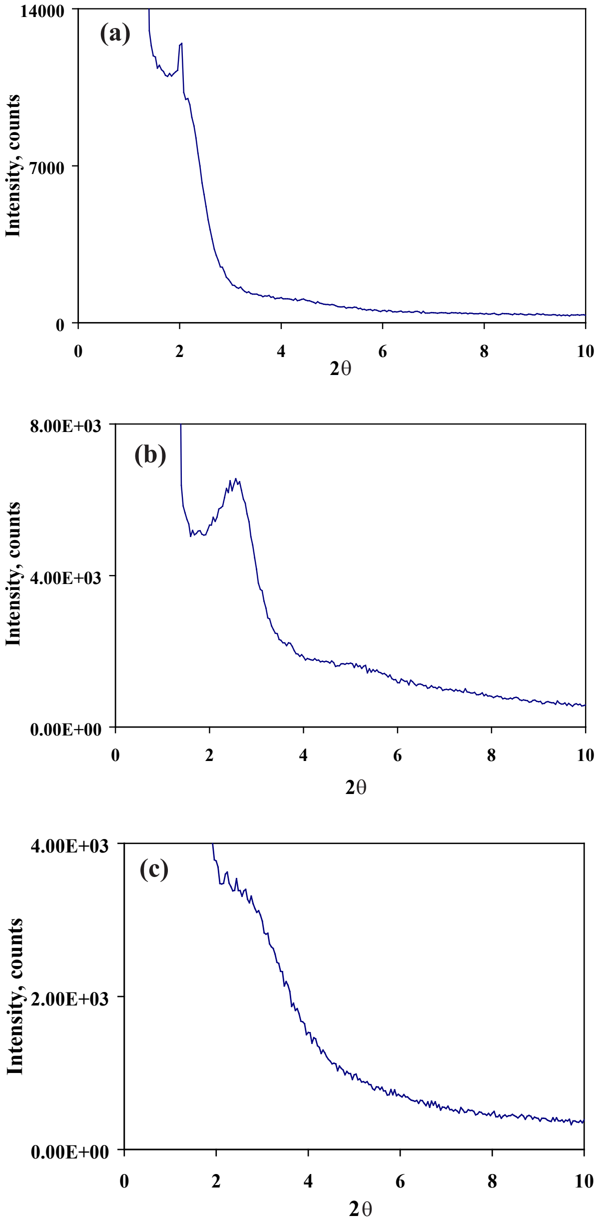

Fig. 1. (a) XRD pattern of mesoporous TiO_2 as synthesized (b) calcined at 823 K (c) calcined at 923 K.

N_2 Adsorption

Nitrogen adsorption-desorption isotherms of mesoporous titania calcined at 823 K are shown in Fig. 2. The isotherms provide information on the texture and porosity of the material. Mesoporous titania shows an isotherm which is intermediate between type II and type IV isotherm with a small and distinct hysteresis loop, which is due to the capillary condensation taking place in side the mesoporous. The observed isotherms can be explained as follows: adsorption at lower relative pressures ($p/p_0 < 0.3$) is due to monolayer adsorption of nitrogen molecules on the walls of mesoporous titania. Thus, a thin layer of adsorbed nitrogen gas on the pore walls was observed at lower relative pressures, which was followed by an inflection ($p/p_0 \sim 0.3$), characteristic of capillary condensation within the walls. This hysteresis loop is due to the capillary condensation which takes place in narrow cylindrical pores of mesoporous titania. The mesoporous titania sample exhibited another sharp inflection at higher relative pressures ($p/p_0 > 0.9$), which can be attributed to macropore filling or to the filling of inter particles. The possibilities of different types of isotherms for mesoporous titania were dealt in literature by various groups [4,6,9-11]. This ambiguous observation based on the poor crystalline nature may be due to the partial collapse of the semicrystallinity of these materials as a result of the thermal treatment at higher temperatures. The BET surface area of the titania was found to be around 400 m^2/g. The pore size distributions calculated on the basis of BJH analysis from the desorption branch of the isotherms show an average pore size distributed around 29 Å.

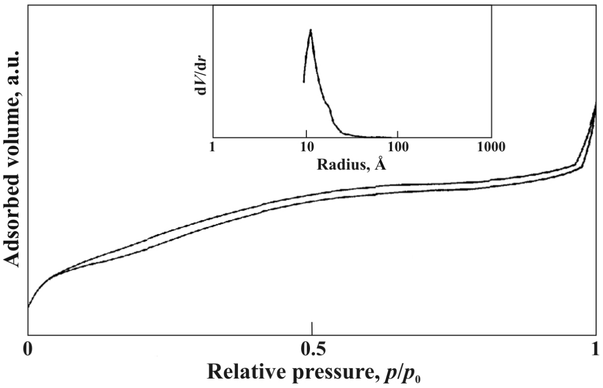

Fig. 2. Nitrogen adsorption-desorption isotherms of mesoporous titania.

Electron Microscope (TEM)

Transmission electron microscopic images have been recorded to observe the formation and morphology of the mesoporous titania. Figure 3 represents TEM image of mesoporous titania calcined at 823 K. As seen from Fig. 3, formation of mesoporous network of titania with a pore size ~3 nm, which is also consistent with pore size measured with N_2 adsorption. Interesting observation is that the mesoporous network remains intact even after calcination unlike the earlier documented literature, where calcination at high temperature results in collapse of mesoporous network.

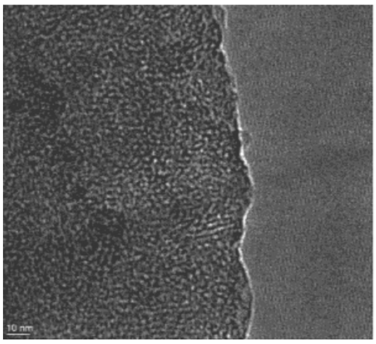

Fig. 3. TEM image of mesoporous titania calcined at 823 K.

Thermal Analysis

Thermal analysis gives an idea on the removal of the surfactant as well as thermal stability of the materials prepared. Figure 4 represents the thermogram of as-synthesized mesoporous titania, which shows mainly four weight loss regions, the first one corresponding to the loss of physi-sorbed water below 373 K. In general, loss of surfactant CTAB can be observed in the temperature range 373-623 K depending on the matrix [1,12-14]. In the case of silica based materials, the weight loss due to the removal of surfactant can be observed in the temperature range 473-573 K. Based on these observations, the second weight loss region in the range 373-550 K can be attributed to the loss of surfactant. The third weight loss above 550 K is due to the removal of the polymer polyethyleneglycol. The final weight loss above 650 K corresponds to the loss of water due to condensation of Ti–OH groups resulting in Ti–O–Ti linkages. It has been observed that titania has thermal stability up to 923 K which is an improvement over the earlier reports where the thermal stability is only up to 773 K. This high thermal stability could be mainly due to the optimized synthesis conditions in a modified procedure.

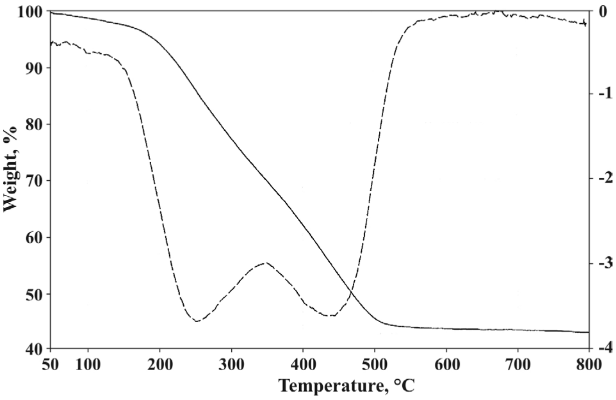

Fig. 4. Thermogravimetric analysis of mesoporous titania.

Conclusions

Mesoporous titania was synthesized using the modified synthetic conditions using CTAB. The synthetic gel was modified with a simple polymer PEG-400. During the approach adopted in the present study, mesoporous titania was synthesized at lower concentrations of the surfactant and the polymer. Mesoporous titania shows thermal stability up to 923 K unlike the earlier reports. This high thermal stability might be attributed to the optimization of the rate of hydrolysis and the condensation processes, which proved to play a vital role in the successful synthesis of the final material.

Acknowledgements

We would like to thank Dr. Benoit Louis for his help in characterization of the material.

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Received 12 February 2007