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Surface and related bulk properties of titania nanoparticles recovered from aramid–titania hybrid films: A novel attempt

Sara J. Al-Omani [a], Ali Bumajdad [a], Fakhreia A. Al Sagheer [a,*], Mohamed I. Zaki [b,**]

[a] Chemistry Department, Faculty of Science, Kuwait University, P.O. Box 5969, Safat 13060, State of Kuwait
[b] Chemistry Department, Faculty of Science, Minia University, El-Minia 61519, Egypt

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ABSTRACT

5 and 10 wt%-TiO_2-containing aramid–titania hybrid films were prepared using sol–gel processing improved by the inclusion of 3-isocyanato-propyltriethoxysilane (ICTOS) to strengthen bonding of the titania species to the polymer backbone and, hence, lessen its agglomeration. The films were thermally degraded by heating at 450 °C in a dynamic atmosphere of air. The solid residues were found by thermogravimetry, X-ray diffractometry and electron microscopy to consist dominantly of uniformly agglomerated rod-like *anatase*-TiO_2 nanoparticles, irrespective of the titania content of the film. The recovered titania particle morphology and surface microstructure were examined by field emission scanning and high-resolution transmission electron microscopy, respectively. Whereas, the particle surface chemistry and texture were assessed, respectively, by means of X-ray photoelectron spectroscopy and N_2 sorptiometry. The recovered titanias were found, irrespective of the film content of titania, to enjoy not only a high temperature (up to 800 °C) stable nanoscopic anatase bulk structure, but also a high-temperature stable surface chemical composition (lattice Ti^{4+} and O^{2-}, and adsorbed OH/CH_x species), (101)-faceted microstructure and highly accessible (145–112 m^2/g), uniform mesoporous texture with average pore diameter in the narrow range of 3.9–6.3 nm. Increasing the calcination temperature up to 1100 °C enhances an *anatase* → *rutile* transition, the extent of which is larger the higher the titania content of the film.

1. Introduction

For several application-worthy surface and bulk properties, titania (TiO_2) is widely used in diverse applications [1]. It is employed as an important ingredient in the manufacturing of pigments, paints, cosmetics, UV blockers, photovoltaics, oxide electronics and advanced sensors [1]. It is, also, used not only as a potential catalyst for a number of technologically and industrially important reactions, but also as an interactive support for a variety of applied metal and metal oxide catalysts [2].

Apart from *brookite*, titania has two more prominent polymorphs, viz. *anatase* and *rutile* [1,3]. These two polymorphs are similar in assuming tetragonal structures, with the *anatase* being of a slightly higher *c*/*a* lattice parameter ratio than the *rutile* [1,4]. Nevertheless, the anatase and rutile titanias have different sets of physical and chemical properties. As for example, *anatase*-TiO_2 is photocatalytically active, whereas the *rutile*-TiO_2 is optically active [1,3]. Due to their different properties, these two polymorphs have their specific domains of applicability [1]. It has, however, been found [5,6] that the TiO_2 polymorphism (*anatase* → *rutile*) is largely controlled by the material particle (crystallite) size. Consistently, the anatase structure has been found [5,6] to be more resistant to the conversion into the rutile structure the smaller the particle size ($<$40 nm) and, hence, the larger the surface/volume ratio of the material. These correlations have facilitated [7] concluding that the energetic driving force of this polymorphic transition of titania is more dictated by the surface energy for nano-sized particles, and that large surface energy stabilizes the otherwise metastable *anatase*-TiO_2 at room temperature. The fact that *anatase*-TiO_2 has a slightly larger band gab energy than *rutile*-TiO_2 (ca. 3.3 and 3.02 eV) [1,8], and that the smaller the particle size the larger the band gab energy [8] would no doubt extend impacts of the particle size to the various applications of titania [1].

Motivated by the above reviewed considerations, considerable effort has been expended over the past decade to synthesize TiO_2 of different gross particle properties (e.g., size, shape, habit, etc.). A variety of synthesis techniques, such as sol–gel [6,9], hydrothermal

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[*] Corresponding author. Tel.: +965 24987076.
[**] Corresponding author. Tel.: +20 102217470.

E-mail addresses: f.alsagheer@ku.edu.kw (F.A. Al Sagheer), mizaki@link.net (M.I. Zaki).

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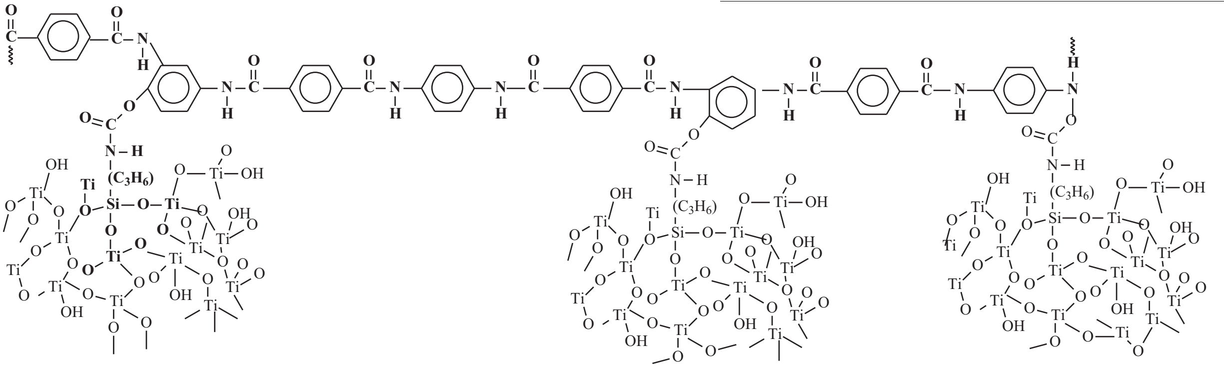
[10], and solvothermal [10] process, have been implemented in this context, and the yielding titanias have been found to assume varied surface and bulk properties [6–12]. In line with this research endeavor, the present investigation is a novel attempt to recover titania by high-temperature oxidative degradation of aramid–titania hybrid films, which has hitherto not been reported in the literature. The chemical structure of the parent film is simplified below analogously to that evidenced for aramid–silica hybrid films [13]. This parent material belongs to an important class of organic–inorganic hybrid materials that exhibits characteristics of both organic polymers and ceramic materials [14,15]. These are easily produced through sol–gel chemistry [16] which allows *in situ* incorporation of metal oxide species in the form of alkoxides of the metals (e.g., Si [13], Ti [17] and Zr [18]) to generate materials of improved chemical and physical properties at low processing temperatures. The narrower distribution of particles and the reduced particle size due to the *in situ* development of the metal oxide network leads to improved mechanical strength and thermal stability [15].



Aramid-Titania (*denoted* x-ArTi)

In the present investigation, aramid–titania hybrid films were synthesized following a modified version of the method described elsewhere [17]. The modification (*vide infra*) was meant to warrant atomic level distribution of the Ti–O species within the organic polymer matrix by facilitating stronger chemical bonding with the polymer components. Subsequently, films thus obtained (with different titania contents) were subjected to thermal analysis in order to determine the appropriate thermal conditions of the titania recovery. Bulk and surface properties of the recovered titanias were assessed by X-ray diffractometry, infrared spectroscopy, electron microscopy, N_2 sorptiometry, and X-ray photoelectron spectroscopy.

2. Experimental

2.1. Materials

5 and 10 wt%-TiO_2-containing aramid–titania hybrid films (*denoted* x-ArTi, where x is either 5 or 10 to refer to the corresponding titania content) were synthesized and, then, thermally degraded by heating in air at 450 °C for 9 or 6 h, respectively. The degradation temperature was chosen based on thermal analysis results of the x-ArTi materials (*vide infra*), whereas the time durations were selected upon trial. The degradation products, *denoted* Dx-ArTi, were subsequently calcined at 500, 800 and 1100 °C for 3 h. The calcination products are denoted, respectively, Cx-ArTi(5), Cx-ArTi(8) and Cx-ArTi(11), where the parenthesized Arabic numeral signifies the calcination temperature applied.

The x-ArTi, whose chemical structure is simplified above, was prepared following a modified version of the recipe reported elsewhere [17]. Briefly, a polyhydroxyamide matrix (aramid) was prepared by reacting a mixture of 1,3- and 1,4-phenylene diamines ($C_6H_4(NH_2)_2$; ≥97%, Aldrich), and 2,4-diaminophenol ($C_6H_3(OH)(NH_2)_2$; 97%, Fluka), in the molar proportions of 12:7:1, respectively, with terephethaloyl chloride ($C_6H_4(OCCl)_2$; 99%, Fluka) in N,N-dimethyl acetamide (DMAC, 99.5%, Fluka) as a solvent. Then, 3-isocyanato-propyltriethoxysilane (ICTOS = $((C_2H_5O)_3Si(C_3H_6)–N{=}C{=}O$; 97%, Fluka) was added (instead of the aminophenyl trimethoxysilane (APTMOS) used in the original recipe [17]) into the polymer solution in order to substitute the pendant hydroxyl groups by pendant alkoxy groups on the polymer chain. Calculated amounts of titanium tetraethoxide ($Ti(C_2H_5O)_4$; 95%, Gelest) were added into the modified polymer matrix, in order to incorporate proportions amounting to 5 and 10 wt%-TiO_2, followed by the addition of 5 wt%-water in the DMAC solvent to effect sol–gel processing. x-ArTi material films thus obtained were casted in Petri dishes, dried at 70 °C overnight, and soaked and washed repeatedly in distilled water to leach out any remains of HCl produced during the polymerization. Eventually, the x-ArTi films were dried at 80 °C for 24 h and, then, at 120 °C for another 24 h, each under vacuum. Reagent proportions, and process conditions, durations and glassware were exactly as detailed in the original recipe [17]. It is worth noting that the modification adopted here, which is confined to replacing the silylating agent APTMOS by the ICTOS, was meant to improve bonding of the titania network homogeneously to the polymer matrix and, thus, lessening largely the titania agglomeration observed previously [17]. This modification was encouraged by (i) a similar modification that was found previously [13] to help preparing aramid–silica hybrid films with homogeneous inclusion of the silica content and (ii) results of preliminary examinations of aramid–titania hybrid films, obtained using APTMOS as a silylating agent, revealing inhomogeneous inclusion of the titania species.

2.2. Characterization methods and techniques

2.2.1. Material bulk

Thermogravimetry (TGA) and derivative thermogravimetry (DrTGA) were carried out, upon heating test materials at 10 °C/min up to 1000 °C, in a dynamic (50 cm^3/min) atmosphere of air, using a model TA-50 Shimadzu automatic analyzer (Japan). X-ray powder diffractometry (XRD) was conducted at room temperature (RT) and $2\theta = 10–80^\circ$ using a model D500 Siemens diffractometer (Germany), equipped with Ni-filtered CuKα radiation ($\lambda = 0.15406$ nm). Crystallite sizing was done implementing the line-broadening technique and Sherrer's formula [19]. To warrant a credible comparison between the results, comparable