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TiO_2 nanoparticle size dependence of porosity, adsorption and catalytic activity

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ABSTRACT

The issue of size-sensitivity of the surface properties of anatase TiO_2 is addressed by examining three samples synthesized by aqueous sol–gel method having different particle sizes on the nanoscale (8–19 nm). A number of characterization methods, namely, X-ray powder diffractometry, infrared spectroscopy, UV–vis diffuse reflectance spectroscopy, sorptiometry and electron microscopy are employed. The data obtained reveal interrelated dependencies of the surface area, porosity, nitrogen and pyridine adsorption capacity and strength, and catalytic methylbutynol decomposition activity on the size of titania nanoparticles. Pertinent size-dependent bulk properties are also revealed and used to account for the changes conceded by the surface properties. Accordingly, going from 19 to 8-nm sized titania particles has been found to stabilize the anatase structure, weaken the surface acidity, and blueshift the UV absorption edge of titania.

1. Introduction

When the size of the material particle becomes smaller down to the nanometer scale, the surface-to-volume ratio and free surface energy increase dramatically, causing specific changes to the material's surface properties [1]. Significant amount of work has been done over the past decade to synthesize titania nanoparticles of various sizes, shapes, and phases using different techniques, since titania nanomaterials serve broad application interests [2]. But, in many reports the attention is mainly focused on elucidation of the gross particle properties (size, shape, phase, etc.) on one hand and measurements related to specific application such as photocatalysis, solar cells, magnetism, sensors, etc. on the other [2,3]. Relatively much less attention seems to have been paid exclusively to the surface properties of nanoparticles such as the surface roughness, kink site density, porosity, chemical reactivity, etc., which clearly hold the key to the effectiveness of these particles in different applications.

Interesting work has been reported in the literature on the synthesis of titania crystals of different shapes such as truncated octahedra or nanosheets having certain surface facets, mainly for enhancing the photocatalytic activity [4]. But naturally occurring or lab made titania surfaces are dominated by the less active (1 0 1) facet since it is thermodynamically the most stable surface indicating low density of coordinatively unsaturated (cu) Ti atoms. Usually, it is understood that the higher the percentage of cu-Ti-atoms the more reactive will be the surface of a crystal in heterogeneous catalytic reactions. Recent reports [5] show that (0 0 1) facet is more reactive than the (1 0 1) facet due to differences in density of cu-Ti atoms thereby differences in surface energies such as $\gamma\{0\,0\,1\}$ ($0.90\,\mathrm{J\,m^{-2}}$) > $\gamma\{1\,0\,1\}$($0.44\,\mathrm{J\,m^{-2}}$). The (0 0 1)-facet has almost double the cu-Ti atoms compared to the (1 0 1)-facet. Also, a recent report discusses the important role of tetrahedral Ti^{4+} sites in the anatase-rutile phase transformation and photocatalytic activity of TiO_2 [6]. Banfield et al. [7] have found that rutile becomes more stable than anatase for particle size >14 nm, and that anatase is thermodynamically stable for particle sizes <11 nm and rutile for sizes >35 nm. Banda et al. [8] have investigated the energetics of the TiO_2 polymorphism (anatase to rutile) by high-temperature oxide melt drop solution calorimetry, and have concluded that rutile is energetically stable for surface area $<7\,\mathrm{m^2\,g^{-1}}$ or particle size >200 nm, whereas anatase is stable for surface area $>40\,\mathrm{m^2\,g^{-1}}$ or size <40 nm. It is obvious from these literature data, and from the fact that anatase and rutile have comparable entropy values [2], that the energetic driving force of polymorphic transitions of titania is more dictated by the surface energy. The smaller the particle size, the larger is the surface energy and more stable is the low-temperature-stable anatase phase. Since in various applications titania nanoparticles of different sizes are used and since surface adsorptions and/or functionalizations define their performance features, it is of great interest to explore the evolution of surface properties with particle size, which is the intent of this work.

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Recently we reported on the surface properties of 8-nm sized particles of anatase TiO_2 prepared by sol–gel method [9]. In the present work, we analyze the size dependence of the various properties by comparing surface properties of 8 nm, 14 nm and 19 nm nanoparticles synthesized by the sol–gel route. The properties examined and compared include the surface area, porosity, adsorption site strength and population, and acid–base site nature and catalytic activity. The relevant bulk properties of titania nanoparticles of the different sizes are also studied.

2. Experimental

2.1. Materials

The three test nanoparticle titanias were TiO_2-8, TiO_2-14 and TiO_2-19, where the suffixed number indicates the XRD-determined average particle (crystallite) size (in nm unit). They were obtained after annealing of an ambient dried titania xerogel at 300 °C, 400 °C and 500 °C for 24 h in air. The xerogel was synthesized by sol-gelation of high purity titanium tetraisopropoxide ($Ti(OC_3H_7)_4$) as detailed earlier [9]. These three TiO_2 samples were kept dry over silica gel till further use and were found by ICP and CHNSO analyses to be >98.9% pure TiO_2 [9].

Surface probe and reactive gas molecules of pyridine (C_5H_5N) and methylbutynol (C_5H_8O) were obtained by expansion of purified vapours of the corresponding liquids (98%-pure products of BDH). Pretreatment and adsorptive gas molecules (O_2, N_2) were 99.9%-pure (El-Hawamddyia/Egypt).

2.2. Methods and techniques

X-ray powder diffractometry (XRD, Jeol JSX-60A, Japan), Transmission electron microscopy (TEM/HRTEM, JSM-3010 Jeol ultra 300 kV microscope, Japan), *in situ* and *ex situ* infrared spectroscopy (IR, Genesis-II FT-IR Mattson, USA), and ultraviolet–visible (UV–vis) diffuse reflectance spectroscopy (DRS, model 2100 UV–vis spectrophotometer, Shimadzu, Japan) were employed to characterize the test samples, as described earlier [9]. The *ex situ* IR spectra were taken of KBr-supported discs of test samples, whereas the in situ spectra were taken of self-supporting wafers of test samples (30 mg/cm^2) mounted in a cell system similar to that described by Peri and Hannan [10]. Procedures adopted for *in situ* sample wafer pretreatment, deareation and expansion of probe molecules of pyridine (Py) and methylbutynol (MBOH), and IR spectra acquisition and handling were as detailed previously [9].

N_2 sorptiometry was performed (at −195 °C) with a model Nova series 2000 Quantachrome automatic sorptiometer (USA), powered with standard Brunauer–Emmett–Teller (BET) [11] and Barrett–Joyner–Halenda (BJH) [12] analytical software for the adsorption/desorption data. The reproducibility of the measurements was better than 98%. Py sorptiometry was gravimetrically carried out at 35 ± 0.5 °C using quartz-glass springs (sensitivity = 0.36 mm/mg; Heräus, Germany) mounted inside an air-thermostated purpose-made gas/vac handling system, and a cathetometer (readability = 10^{-4} cm; The Precision Tool & Instrument Co./Thoronton Heath/UK) for spring elongation measurements. Test sample pretreatment and degassing, as well as gravimetry measurements were undertaken as reported previously [9].

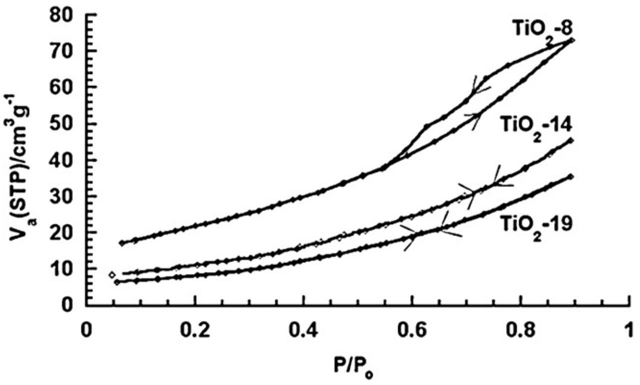

Fig. 1. N_2 adsorption–desorption isotherms determined (at −195 °C) on the test titanias.

Temperature-programmed desorption (TPD) was conducted on heating of Py/titania up to 700 °C (at 10 °C/min), using a ChemBET 3000 (Quantachrome/USA). For this experiment, a (1–2)-g portion of test sample was first degassed in a stream of N_2 atmosphere at 120 °C for 2 h, and then 24 h exposed at room temperature (RT) to a saturation pressure of Py vapor, facilitated by a specially designed manipulator, in order to establish the Py/titania study system.

3. Results and discussion

3.1. Surface texture and microstructure

Fig. 1 compares N_2 adsorption–desorption isotherms determined on the three test titania samples. It is obvious from the figure that the three isotherms are similarly type-IV, except that the isotherm determined on TiO_2-8 exhibits a distorted type-H2 hysteresis loop [13]. These results indicate that the test samples are porous, and that only TiO_2-8 is distinguished by pore diameters facilitating the capillary condensation implied by the hysteresis loop. The H2-typeness of the hysteresis loop exhibited by TiO_2-8 is attributable to a difference in mechanisms of condensation and evaporation processes occurring in pores with narrow necks and wide bodies (often referred to as ink bottle pores) [13a], but it is now recognized that this provides an over-simplified picture and the role of network effect must be taken into account [13b].

Processing of the N_2 adsorption data by means of the BET [11] and BJH [12] methods resulted in the surface textural characteristics set out in Table 1. It is obvious from the table that values of the specific surface area (S_{BET}), the cumulative surface area (S^{cum}), the total pore volume (V_p^t) and the pore cumulative volume (V_p^{cum}) are inversely proportional to the average particle size of the test titania samples. This trend of variation is quite compatible with expectation [13]. On the other hand, the closeness of the C_{BET} constant values (Table 1) accounts for a closely similar surface chemistry for the test samples. The fact that the calculated geometric surface area (S_g) is higher than the corresponding N_2-determined surface

Table 1
Surface textural characteristics as derived from N_2 adsorption data.

Titania	$S_{BET}/\pm 2$ m^2 g^{-1}	C_{BET}	S^{cum}/m^2 g^{-1}	S_g[a]/m^2 g^{-1}	$f = S_{BET}/S_g$	V_p^t/cm^3 g^{-1}	V_p^{cum}/cm^3 g^{-1}	Average pore diameter (nm)
TiO_2-8	80	95	108	191	0.42	0.1128	0.1295	6.65
TiO_2-14	41	86	63	107	0.38	0.0701	0.0821	5.00
TiO_2-19	30	103	48	79	0.38	0.0549	0.0644	5.03

[a] S_g is the geometric surface area calculated adopting an idealized cubic model, pychnometrically determined density of test samples ($\rho = 3.94 \pm 0.01$ g/cm^3) and the XRD-determined average crystallite size (D), implementing the formula $S_g = 6/(\rho/D)$ [9a].