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LETTER

Alcohol washing as a way to stabilize the anatase phase of nanostructured titania through controlling particle packing

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In the as-prepared condition most nanostructured ceramic materials are in their metastable state and on further heat treatment they convert to the relatively more stable phase [1–7]. Titania is no exception in this regard [3–7], upon heat treatment the metastable anatase phase of titania transforms to the stable rutile phase. The exact temperature of transformation depends on many factors such as primary particle size, cation content and packing and coordination of primary particles in the aggregate. In the case of titania the metastable anatase phase finds several interesting applications in the fields of photo catalysis, ceramic membranes, photo voltaics, and optics [8–11]. Study of anatase-to-rutile transformation in titania is not only of great commercial importance but also of immense theoretical significance [1–7, 12–26]. Several commercial applications use titania-based systems and devices at elevated temperatures [4–6, 27] and preventing the anatase-to-rutile transformation is important to retain the useful properties of the metastable anatase phase [4–6]. Even for applications without phase sensitivity, controlling anatase-to-rutile transformation is important because this transformation is always accompanied by drastic grain growth, porosity, and surface area reduction and also results in the destruction of the "nanostructuredness" of the system as a whole [4–6]. From 1993, in a series of papers, it has been postulated by Kumar and others that in metastable-to-stable transformations like the anatase-to-rutile transformation, critical-nuclei-size-effect limits our ability to carryout this transformation without appreciable particle growth [4–6, 12, 17, 18, 25, 26, 28]. Later this claim has been supported by several other researchers [21, 23]. This means that one of the ways to preventing or slowing down anatase-to-rutile transformation is to make sure that anatase particles do not grow to reach the critical-nuclei-size. This can be achieved by controlling packing and coordination of primary particles within the aggregates. In two separate studies Kumar et al. [12, 29] have shown that the influence of packing and coordination on the anatase-to-rutile phase transformation. Gels with loosely packed textures transformed slower than well-packed gels [12, 29]. Also loosely packed titania gels gave higher activation energy (358 kJ/mol) for the transformation compared to well-packed gels (213 kJ/mol) [29].

It has been shown by Nair et al. [30–32] that washing of hydrogels with alcohol could be an effective technique to influence the phase transformation behavior of nanostructured oxides through controlling packing and coordination. Nair et al. have noticed that in the case of alumina [30], $La_2Zr_2O_7$ [31], and lanthana-alumina systems [32], alcohol washing increased the amorphous to crystalline (metastable-to-stable) transformation temperature. They have also observed higher surface area and pore volume in the case of alcohol-washed samples compared to water-washed samples. They have attributed this surface area and pore-structure improvement and the shift in transformation temperature to lower level of packing and coordination in

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alcohol-washed gels compared to water-washed gels due to the lower surface tension of alcohol compared to water [30–32].

There are several more studies in the literature that address the influence of washing and drying of oxide gels, including titania gels, on phase and textural evolution [33–36]. Youn et al. have reported the influence of alcohol washing on the amorphous to anatase crystallization behavior of titania [33, 34] and explained the difference solely based on the presence of oxo-alkoxide groups. However, in their study there was no attempt to understand the possible contributions of other phenomena such as differences in density of the gel network due to the difference in surface tension of water and alcohol during drying of the gels. It is important to note that in their FT-IR studies Nair et al. [30–32] did not find the presence of ethoxide groups in alcohol-washed gels. However, in the case of zirconia gels, Mercera et al. [35] attributed the higher textural stability of zirconia samples to the slower polycondensation during gelation due to the presence of ethoxide groups. In the case of ethanol-washed alumina, Kaliszewski and Heuer [36] also attributed higher porosity and surface area to slower polycondensation due to the presence of ethoxide groups.

None of the above mentioned studies have examined the influence of alcohol washing on the anatase-to-rutile phase transformation of titania. It should be noted that a recent report on the influence of alcohol washing on titania did not study anatase-to-rutile transformation behavior [33, 34]. Moreover, they have ignored the importance of the influence of the surface tension of the pore-fluid during drying on the final packing and coordination of primary particles in the gel. In the present article, we compare the texture and phase transformation behavior of alcohol-washed and water-washed titania gels and study the influence of packing on the anatase-to-rutile phase transformation behavior.

Titania gel was prepared by the hydrolysis of dilute solutions of commercial titanium isopropoxide (Wako Chemicals, Japan) in propane-2-ol (isopropyl alcohol) under atmospheric condition. The hydrolysis was carried out as follows: 0.18 mol of the alkoxide was first dissolved in 350 g (5.8 mol) of propane-2-ol and the solution was added drop-wise to 35000 g (ca. 35 L) of distilled water with vigorous stirring at room temperature. After separation of the precipitated gel by decantation and centrifugation, the precipitate was divided into two portions, the first portion was washed with a total of 5 L of deionized water in five steps. The second portion was washed with a total of 5 L of propane-2-ol in five steps. Both water-washed and alcohol-washed gels were dried in an oven at 110 °C for 24 h and designated as WWOD and IWOD, respectively. All the samples were calcined at 400, 700, and 800 °C for 8 h with a heating rate of 5 °C min^{-1}. X-ray diffraction (XRD) patterns were recorded on a MAC Science MPX 18 using Cu Kα radiation with a nickel filter. The size of the crystallites present in the anatase phase was calculated using Sherrer relationship: $D_{hkl} = K\lambda/(B_{hkl}\ \mathrm{Cos}\theta)$, where B_{hkl} is the width of the peak at half maximum and λ is the wave length of Cu Kα radiation. A value of 0.9 is used for K in this study. The fractions of rutile present in the samples were calculated using the following equation [26, 37]: $W_\mathrm{R} = 1/(1 + 0.8\ (I_\mathrm{A}/I_\mathrm{R}))$. Thermal gravimetry and differential thermal analysis (TG-DTA) were carried out on a MAC Science TG-DTA 2100 instrument with a heating rate 10 °C min^{-1} under a flow of 100 $\mathrm{cm}^3\ \mathrm{min}^{-1}$ dry air. The infrared (IR) spectra were measured using a Shimadzu FTIR-8500 infrared spectrophotometer using the usual KBr pellet technique. Specific surface area was measured by BET method based on the adsorption of N_2 at 77 K using a Belsorp 36 of BEL Japan. Pore size distribution was evaluated by analyzing the N_2 desorption isotherms according to the Dollimore–Heal method (D–H method) [38].

From Table 1 it can be seen that amorphous-to-crystalline (anatase) transformation takes place in the temperature range of 400–450 °C. The water-washed gels (WWOD) showed a lower transformation temperature compared to alcohol-washed samples (IWOD). A similar difference can also be seen for the anatase-to-rutile transformation temperature. WWOD gels transformed already at 816 °C compared 853 °C for IWOD samples. XRD data given in Fig. 1 and quantitative estimates of crystallite size and phase composition given in Table 2 support this finding. At 700 °C IWOD sample is predominantly anatase, whereas WWOD samples show more than 50% rutile phase. Also WWOD contains larger rutile crystallites compared to IWOD samples. Differences in pore volume and surface area are given in Fig. 2 and Table 3. Both pore size and pore volume is lower for WWOD samples compared to IWOD samples. This is a clear indication of higher degree of packing in WWOD. High degrees of packing will increase the number of particle-to-particle contact (coordination) in the dried gels. In addition to the obvious differences in pore volume and pore size, this difference in packing and coordination can also influence surface area, crystallite size and phase transformation behavior. It is

Table 1 Phase transformation temperature obtained from DTA of TiO_2 samples after water washing (WWOD) and alcohol washing (IWOD)

Samples	Amorphous-to-anatase transformation (°C)	Anatase-to-rutile transformation (°C)
WWOD	403	816
IWOD	448	853

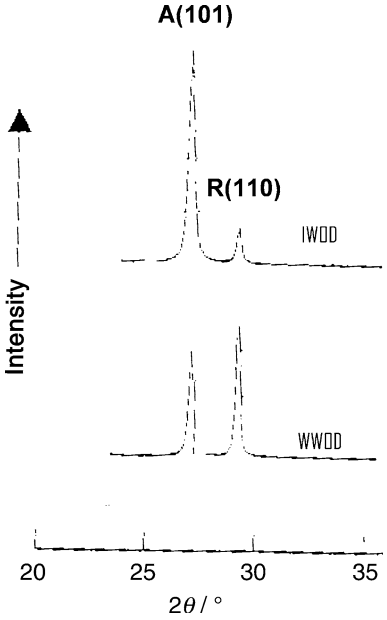

Fig. 1 XRD patterns of water-washed (WWOD) and alcohol-washed (IWOD) samples heated at 700 °C for 8 h

important to note that critical-nuclei-size-effect is predominant during the process of conversion of as-prepared anatase to rutile through heat treatment. In other words when we heat treat as-prepared anatase it will convert to rutile only after growing to a certain size called the critical-nuclei-size and it can be determined as follows [26, 28, 39]:

The total energy change, G_{Total} when phase "A" transforms to "R" can be written as:

$$G_{\mathrm{Total}} = \frac{4}{3}\pi r^3 \Delta G_{\mathrm{CHEM}} + \frac{4}{3}\pi r^3 \Delta G_{\mathrm{STRAIN}} + 4\alpha\pi r^2 \gamma_{\mathrm{AR}} + 4\beta\pi r^2 \gamma_{\mathrm{RG}} + 4\delta\pi r^2 \gamma_{\mathrm{RR}} \quad (1)$$

Differentiating Eq. 1 with respect to the radius of the embryo, r and equating it to zero at maxima of the function will yield the critical-nuclei-size, r_c.

$$r_c = -2\left[\frac{\alpha\gamma_{\mathrm{AR}} + \beta\gamma_{\mathrm{RG}} + \delta\gamma_{\mathrm{RR}}}{\Delta G_{\mathrm{CHEM}} + \Delta G_{\mathrm{STRAIN}}}\right] \quad (2)$$

where G_{CHEM}, G_{STRAIN}, γ_{AR}, γ_{RG}, γ_{RR} are the Gibbs free energy, strain energy, anatase–rutile interfacial energy, rutile–air interfacial energy and rutile–rutile grain-boundary energy, respectively. α, β, and δ are the fractions of interfacial area contributed by anatase–rutile, rutile–air, and rutile–rutile interfaces, respectively. The reason why critical-nuclei-size-effect is predominant during heat treatment is because unlike solution–sol–gel synthesis we have very little control over different surface energies and therefore size of the critical-nuclei is more or less determined only by G_{CHEM}.

There are two entirely different mechanisms proposed in the literature for explaining the difference between water-washed and alcohol-washed gels; one based on the difference in packing and coordination, caused by the difference in drying stress, of the primary particles in the gels advanced by Kumar and colleagues [12] and the other based on the differences in polycondensation due to the presence of alkoxide groups [35, 36]. However, in the present case FT-IR data did not show any appreciable difference between WWOD and IWOD gels with respect to the presence of alkoxide groups. Therefore, it is reasonable to explain the observed difference in phase transformation behavior, surface area and crystallite size based on the difference in packing of primary particles caused by the difference in drying stresses. It has been shown repeatedly that, either through washing with liquids with surface tensions different from that of water or through other techniques such as peptization followed by drying [12] or other drying techniques such as freeze drying [40], there is a clear relationship between degree of packing and phase transformation behavior.

A schematic representation of the difference in packing and coordination is given in Fig. 3. Primary particles in WWOD gels are relatively well-packed compared to IWOD samples. Influence of the surface tension of the pore fluid on stress experienced during drying of porous gels has been clearly demonstrated in the literature [41]. WWOD gels experience much larger drying stress due to higher surface tension of water (around 70 dyn cm^{-1}) compared to 23 dyn cm^{-1} for isopropyl alcohol. For a given pore diameter WWOD gels will experience drying stress which is almost 3 times higher than that experienced by IWOD gels. Therefore, pore fluids with higher surface tension will cause the formation of well-packed structures with lower porosity and surface area. Lower surface area means higher fraction of solid–solid interface compared to solid–gas interface. This will energetically favor smaller critical-

Table 2 Phase composition and crystallite size (in the anatase phase) for different calcination temperatures

Sample	400 °C			700 °C			800 °C
	Phase	Wt% of anatase	Cryst. size of anatase (nm)	Phase	Wt% of rutile	Cryst. size of rutile (nm)	Wt% of rutile
WWOD	A	100	9	R + A	53	83	100
IWOD	A	100	11	A + R	12	47	100

A anatase, *R* rutile

Fig. 2 Pore size distribution obtained from N_2 adsorption isotherms of water-washed (WWOD) and alcohol-washed (IWOD) samples

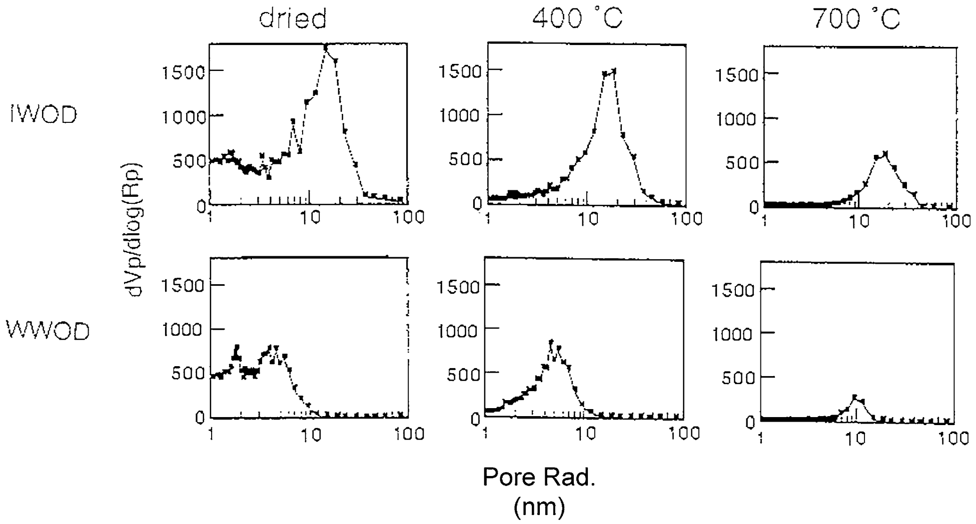

Table 3 BET surface area and total pore volume of dried gels and the gels heated at 400 and 700 °C

Sample	Dried gel	400 °C	700 °C	
	V_p (cm^3/g)	V_p (cm^3/g)	S_{BET} (m^2/g)	V_p (cm^3/g)
WWOD	0.60	0.33	14	0.08
IWOD	1.23	0.73	39	0.27

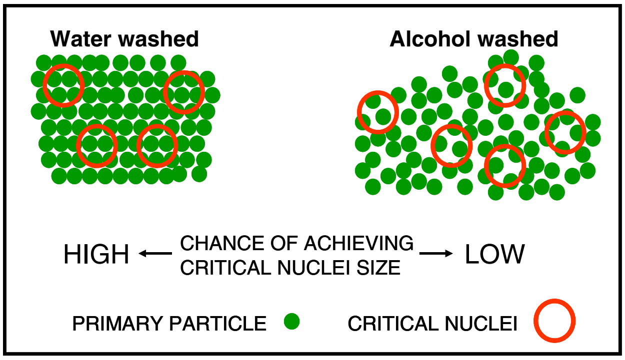

Fig. 3 Schematic representation of packing of primary particles in water-washed and alcohol-washed samples

nuclei and hence faster phase transformation [12]. In the present case the fraction of rutile–rutile interface will be relatively larger than rutile–air interface ($\beta < \delta$) and also we know that $\gamma_{RG} > \gamma_{RR}$, according to Eq. 2 critical-nuclei-size will be slightly smaller than loosely packed gels. Even though WWOD may have a lower critical-nuclei, higher coordination will enhance crystallite growth due to higher particle–particle contact points [12, 42].

In summary it has been shown that replacing water with lower surface tension pore fluids like isopropyl alcohol will enable us to enhance the thermal stability of sol–gel derived titania. Lower packing density of alcohol-washed gels will exhibit slower phase transformation and crystallite growth. Alcohol-washed gels also retained higher surface area and porosity. In addition our results point to the importance of critical-nuclei-size-effect in the metastable-to-stable phase transformation of nanostructured anatase titana.

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