MATERIALS CHEMISTRY COMMUNICATION

Physical stabilization of anatase (TiO_2) by freeze-drying

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The anatase phase of titania has been stabilized without chemically modifying the system, by changing the level of packing within the aggregates by freeze-drying the water-washed precipitate obtained by the hydrolysis of titanium isopropoxide. After calcination at 700 °C for 8 h, freeze-dried samples showed more than 97% anatase phase with a surface area and porosity of 29 $m^2 g^{-1}$ and 37% respectively. The oven-dried samples showed a surface area and porosity of 5 $m^2 g^{-1}$ and 10% respectively.

The anatase modification of titania is an important material for catalysis.[1] Anatase is a metastable phase and it will transform irreversibly to the stable rutile phase.[2–5] For many applications this transformation is not favoured, for two main reasons: (1) anatase has distinctly better catalytic properties than rutile,[1] and (2) this transformation always results in a dense (non-porous) rutile phase, which is not useful as a catalyst or as a ceramic membrane material.[5,6] It is generally observed that the anatase-to-rutile transformation temperature depends on many factors like preparation conditions, nature of the precursor, minor impurities, morphology of the primary particles *etc.*[6] Almost all the attempts to stabilize the anatase phase have been based on changing the chemistry of the system.[1,6,7] Even in those studies in which a chemical modification was not the primary aim, the stabilization technique ultimately resulted in modifying the chemistry of the system.[8,9] However, the degree of modification is thought to be much smaller than for other chemical methods of stabilization.[8,9] In this paper we report, for the first time, a purely physical means of stabilization of the anatase phase. The major advantage of this is that unlike chemical modification, this technique will not change the chemistry of the system, which means that the catalytic properties are not changed.

The anatase-to-rutile transformation is a nucleation growth type of transformation and the temperature and rate at which it happens, from a physical point of view, depends on how fast the primary particles of the anatase phase sinter together to reach the critical nucleus size.[10] From circumstantial evidence, it is expected that the critical nucleus size of rutile is at least three times larger than the crystallites present in the anatase phase.[11] This means that if sintering of anatase particles is retarded by a suitable technique (the probability of reaching the critical nucleus size is lowered), we can retain a high porosity and surface area as well as retard the transformation to rutile. In this study we have retarded the sintering by effectively decreasing the packing of anatase particles by freeze-drying.

Table 1 Effect of drying method on the phase transformation temperature and BET surface area

	phase transformation temp./°C[a]		surface area/$m^2 g^{-1}$	
method	am.→ana.	ana.→rut.	400 °C	700 °C
oven-dried	399	727	116 (51)[b]	5 (10)
freeze-dried	416	895	75 (57)	29 (37)

[a]Phase transformation temperaures from amorphous (am.) to anatase (ana.) and anatase to rutile (rut.) obtained from exothermic peaks of DTA curves. [b]Values in parentheses show porosities (%) evaluated by using total N_2 adsorption amounts and densities of titania (3.8 g ml^{-1} for oven-dried and 400 °C heated sample and freeze-dried samples, 4.2 g ml^{-1} for oven-dried and 700 °C heated sample).

Titania powder was prepared by the hydrolysis of titanium isopropoxide (Wako Chemicals, Japan). The alkoxide (0.18 mol) was dissolved in 350 g (5.8 mol) of isopropyl alcohol and this solution was added dropwise to 350 g of distilled water under vigorous stirring at room temperature. After separation of the precipitated gel by decantation and centrifugation, the precipitate was washed five times with a total of 5 l of deionized water. This washed precipitate was then divided into two portions: one portion was dried in an oven at 110 °C for 24 h (designated as WWOD); the other portion was freeze-dried (WWFD).

From the thermal analysis data it was found that both samples were amorphous in the as-prepared state and on heating transforms first to anatase and then to rutile. Table 1 gives the DTA transformation temperatures and the textural properties (surface area and porosity) of the oven-dried and freeze-dried samples. As expected, both transformation temperatures, amorphous-to-anatase and anatase-to-rutile, are higher for the freeze-dried samples. During drying the WWOD samples experience a large compressive stress, owing to the surface tension of the pore fluid, compared to the WWFD samples. Therefore the level of packing of primary particles within the aggregate and also the packing of aggregates themselves will be higher compared to the WWFD. It should be noted that during freezing, the first step in the freeze-drying process, the WWFD samples will also experience compressive stresses similar to drying stresses.[12,13] However, this stress will not be acting throughout the sample and, moreover, the possibility for the primary particles to rearrange during freezing is much lower compared to the rearrangement during the oven-drying of WWOD. A lower level of packing will lead to large porosity (Table 1) and a broad pore size distribution with a higher average pore size. This can be seen from the pore size distribution data given in Fig. 1. The average pore size of WWOD samples is lower than that of WWFD. Moreover, WWOD samples show a broader pore size distribution with some pores in the microporous (pore radius <1 nm) range.

A lower level of packing in WWFD samples will result in a lower number of particle–particle contacts and this in turn results in slower particle growth. Therefore WWFD samples will transform more slowly than WWOD samples. Fig. 2 shows XRD patterns of the samples heated at 400 and 700 °C. After heating at 400 °C for 8 h both the samples show the typical

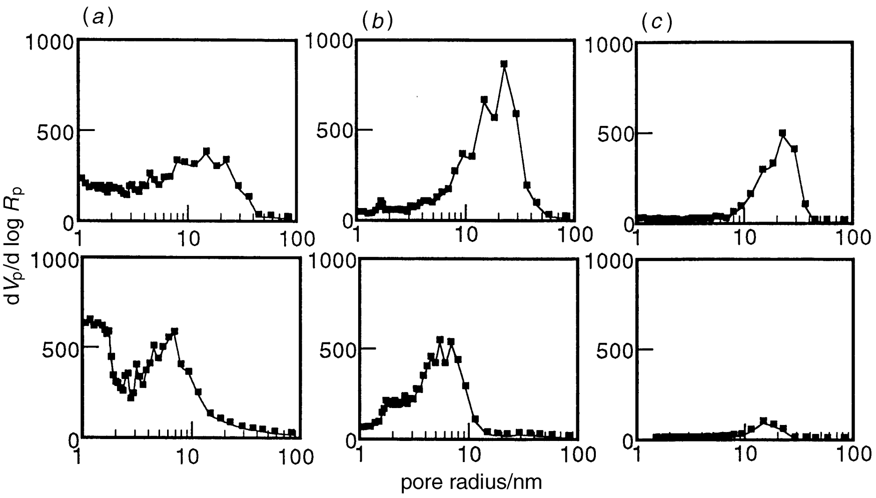

Fig. 1 Pore size distributions of WWOD and WWFD before heating (*a*) and after heating to 400 °C (*b*) and 700 °C (*c*). Upper traces: freeze-dried; lower traces: oven-dried samples

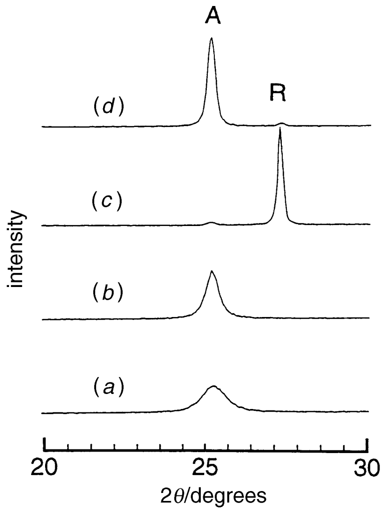

Fig. 2 X-Ray diffraction patterns of the titania samples: (*a*) WWOD heated at 400 °C; (*b*) WWFD heated at 400 °C; (*c*) WWOD heated at 700 °C; (*d*) WWFD heated at 700 °C. A = anatase, R = rutile

anatase pattern [Fig. 2 (*a*) and (*b*)], but at 700 °C WWFD [Fig. 2(*d*)] practically remains as anatase and WWOD [Fig. 2(*c*)] transforms to rutile.

The higher surface area of WWOD at 400 °C is probably due to the presence of micropores in the WWOD. However, the WWFD sample shows higher porosity indicating a lower level of packing. At 700 °C WWFD has a much higher surface area (29 m^2 g^{-1}) and porosity (37%) with more than 97% anatase phase. From the above results it can be seen that freeze-drying is a very effective way to stabilize the catalytically important anatase phase with high surface area and porosity at relatively high temperatures.

References

1 K. Foger and J. R. Anderson, *Appl. Catal.*, 1986, **23**, 139.
2 R. D. Shannon and J. A. Pask, *J. Am. Ceram. Soc.*, 1965, **48**, 391.
3 C. N. R. Rao, *Can. J. Chem.*, 1961, **39**, 498.
4 F. Dachille, P. Y. Simens and R. Roy, *Am. Mineral.*, 1968, **53**, 1929.
5 K-N. P. Kumar, K. Keizer, A. J. Burggraaf, T. Okubo, S. Morooka and H. Nagamoto, *Nature* (*London*), 1992, **358**, 48.
6 K-N. P. Kumar, K. Keizer and A. J. Burggraaf, *J. Mater. Chem.*, 1993, **3**, 1141.
7 Y-S. Lin, C-H. Chang and R. Gopalan, *Ind. Eng. Chem. Res.*, 1994, **33**, 860.
8 K-N. P. Kumar, Jalajakumari Kumar, K. Keizer, T. Okubo, M. Sadakata and J. Engell, *J. Mater. Sci. Lett.*, 1995, **14**, 1784.
9 K-N. P. Kumar, *Appl. Catal.*, 1994, **119**, 163.
10 K-N. P. Kumar, Jalajakumari Kumar and K. Keizer, *J. Am. Ceram. Soc.*, 1994, **77**, 1396.
11 K-N. P. Kumar, *Scr. Metall. Mater.*, 1995, **32**, 873.
12 G. W. Scherer, *J. Non.-Cryst. Solids*, 1993, **155**, 1.
13 J. Kumar, PhD Thesis, University of Twente, The Netherlands, 1995.

Communication 7/01755C; *Received* 13*th March*, 1997