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LETTER

Phase stabilizing effects of phosphates and sulfates on nanocrystalline metastable tetragonal zirconia

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Introduction

Sulfated zirconia has gained a lot of interest due to the ability to catalyze a wide range of organic reactions such as isomerization of *n*-butane [1], synthesis of derivatives of 1,5-benzodiazepine and diaryl sulfoxides [2], and benzylation of toluene [3]. The catalytic properties of phosphated zirconia are likewise well-known [4–6]. Phosphates and sulfates are known to stabilize the tetragonal and cubic phase in zirconia, but the effect is not yet fully understood. Several authors have proposed that the stabilization is a crystal size effect, where the surface free energy difference between the tetragonal and monoclinic phase for sufficiently small crystals exceed the bulk free energy difference between the two phases [7, 8]. Other authors ascribe the stabilization to the presence of anionic impurities such as SO_4^{2-}, PO_4^{3-} and Cl^- [9–11]. The theory based on anionic stabilization of the tetragonal phase is the most commonly accepted. This investigation specifically addresses the surface effect of the stabilization by sulfate and phosphate on tetragonal zirconia, by experimental removal of the crystal size effect.

Experimental

All chemicals were supplied by Sigma–Aldrich Inc. (St. Louis, MO, USA) and used as received. Highly porous nanocrystalline tetragonal zirconia powders were synthesized as previously described [12] by controlled hydrolysis of $ZrOCl_2$ followed by careful calcination. The t-ZrO_2 powders are extremely porous and have specific surface area of ~150 m^2/g. The synthesized t-ZrO_2 powders were kept in water-free environment for further treatment.

Surface modification

In the inert atmosphere of a glovebox, 1 g metastable tetragonal zirconia was stirred for 150 min with 10 mL anhydrous methanol and 1 mL of either 99.99% phosphoric acid or concentrated sulfuric acid. The mixture was filtered and the zirconia powder was washed twice with anhydrous methanol and dried at RT in the glovebox. Four samples were prepared with tetragonal zirconia, originating from two different batches. For reference a small sample of the surface modified zirconia was mixed with a methacrylic monomer mixture (bisphenol-A diglycidyl ether dimethacrylate, urethane dimethacrylate, and triethylene glycol dimethacrylate—Bis-GMA/UDMA/TEGDMA, 36/44/20 wt%) and a photo polymerization system (champhorquinone and ethyl 4-dimethylamino benzoate—CQ/DABE both 0.5 wt%). A sample was placed between two glass plates and cured for 2 min using blue light (1,100 mW) from a Bluephase® light probe (Ivoclar Vivadent, Liechtenstein). The polymer matrix prevents the tetragonal crystals from undergoing phase transformation. Such samples are termed matrix dispersed zirconia. The cured samples were then subjected directly to the X-ray diffraction (XRD) measurement for phase analysis.

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Results and discussion

The phosphor and sulfur content in the phosphated and the sulfated samples were by XPS (K-alpha Monochromated, XPS spectrometer, Thermo Fisher Scientific Inc., Waltham, MA United States) analysis determined to ~5 and ~4 atom%, respectively. Due to the careful washing in the preparation step, it is assumed that measured amounts represent ionic binding of SO_4^{2-} and PO_4^{3-} to the surface. The reference sample did not contain either phosphor or sulfur.

The recorded X-ray diffraction (XRD) patterns (STOE & Cie GmbH, Darmstadt, Germany) for the reference sample, the phosphated and the sulfated samples are illustrated in Figs. 1, 2, and 3. For all three samples the XRD patterns are recorded in air and in water. Furthermore matrix dispersed zirconia samples were analyzed using XRD. From Fig. 1 it is seen that the reference sample only contains traces of the monoclinic phase prior to exposure to humidity and the tetragonal 101 reflection of zirconia at $30.2° = 2\theta$ is dominating. Broad peaks in the XRD patterns are a result of small crystal sizes. The powder is very moisture sensitive and a few seconds of air exposure induces the martensitic tetragonal to monoclinic (t → m) phase transformation [13]. After air exposure the two monoclinic reflections (−111 and 111) grows in intensity and the (101) reflection decreases, indicating a t → m transformation. The monoclinic volume fraction (v_m) is calculated following a procedure proposed by Toraya et al. [14] to ~0.68. After addition of a drop of water to the XRD sample the monoclinic reflections becomes even more dominating ($v_m \approx 0.84$). For both the phosphated and the sulfated samples no change in XRD patterns are observed even with water addition and v_m is calculated to ~0.5 both before and after exposure to humidity. Thus, phase transformation does not occur in any of the samples. However, it also shows phase transformation of some of the zirconia crystals during the surface modification procedure. This is presumably due to water in the phosphoric and sulfuric acids or condensation reactions of the two acids with OH groups on the zirconia surface.

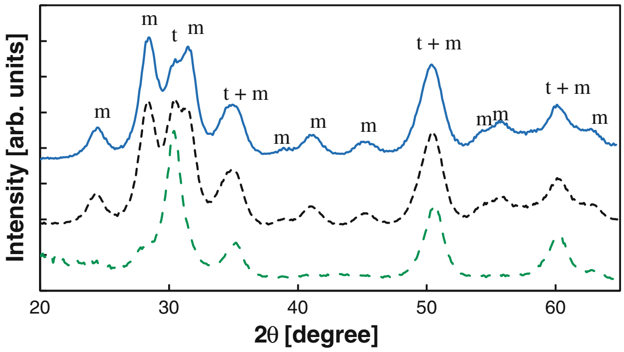

Fig. 1 Unmodified zirconia in resin (*dashed green*), exposed to ambient atmosphere (*dotted black*) and water (*blue*)

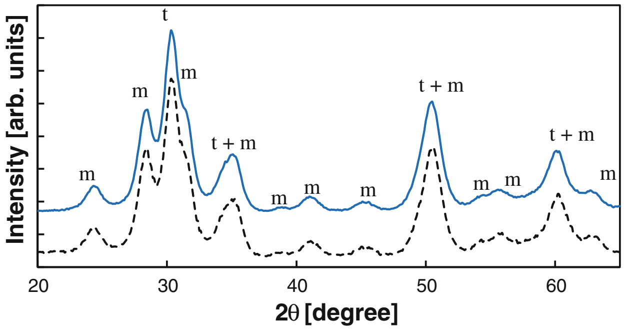

Fig. 2 Phosphated zirconia exposed to ambient atmosphere (*dotted black*) and water (*blue*)

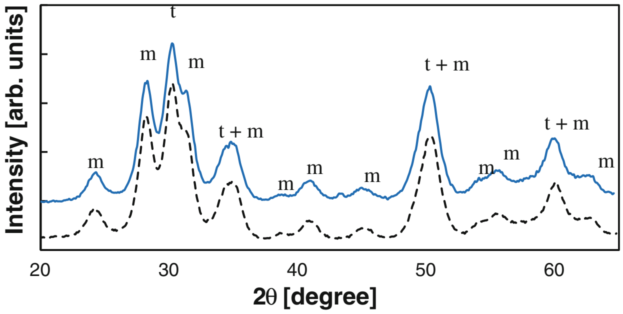

Fig. 3 Sulfated zirconia exposed to ambient atmosphere (*dotted black*) and water (*blue*)

It has been speculated that the stabilizing effect of sulfate and phosphate on the tetragonal phase at RT is due to a retardation of particle growth during the calcination [15]. However, in the present study the zirconia is sulfated or phosphated after calcination and thus the crystal size is the same for neat and surface treated specimens. The crystal size of the reference sample was calculated by the use of Scherrer equation [16] to ~6 nm which, as expected, did not change as a result of the modification with phosphoric or sulfuric acid in any of the samples. The crystal size was confirmed by the transmission electron microscope analysis (FEI Technai, FEI Company, Hillsboro, OR USA)—showing that all the samples indeed are composed of very small, heavily agglomerated 6–8 nm nanocrystallites, which are interconnected and make three dimensional porous networks of up to 1.5–2.0 µm. From the TEM images could further be concluded that the morphology of the zirconia powder does not change as a result of modification with either phosphoric or sulfuric acid (see Fig. 4).

The results support that the phase stabilization is an anionic stabilization effect and not crystal size effect. Mekhmer and Ismail [10] found that calcination of phosphated monoclinic zirconia does not influence the crystal

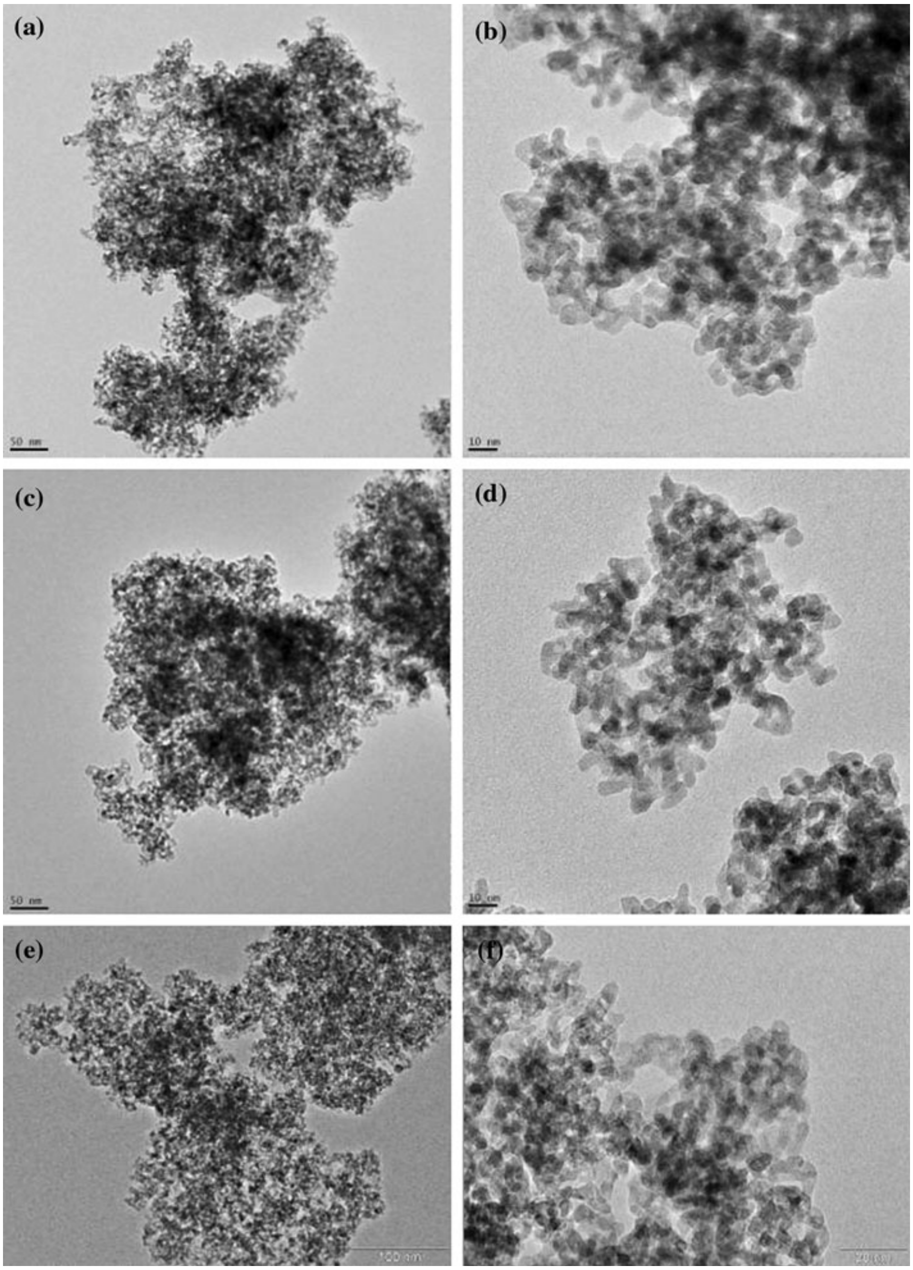

Fig. 4 TEM images of **a**–**b** phosphated sample, **c**–**d** sulphated sample, and **e**–**f** reference sample

phase and furthermore that the zirconia remained monoclinic upon calcination, similarly to the unmodified zirconia sample. Thus, PO_4^{3-} ions are capable of hindering phase transformation but are not capable of inducing a monoclinic to tetragonal phase transition.

Different mechanisms are proposed for the t → m phase transformation. A number of these are based on reaction with water on the crystal surface. Today, it is commonly accepted that the existence of metastable tetragonal zirconia at RT is due to the stabilizing effect of oxygen vacancies in the crystal lattice and that the phase transformation of pure tetragonal zirconia can be initiated by reaction with water [17]. Within this framework SO_4^{2-} and PO_4^{3-} ions prevents water molecules from reacting with the zirconia surface and/or retards the migration of OH^- ions into the oxygen vacancies and thereby prevents the hydrolytic degradation of tetragonal zirconia. Alternatively SO_4^{2-} and PO_4^{3-} ions both change the surface energy and thereby retard the transformation. It has been proposed that water adsorbed on the tetragonal zirconia surface reduces the surface energy difference between the tetragonal and the monoclinic phases [18, 19]. Such a surface energy reduction will reduce the critical size of the tetragonal crystals and thereby induce the t → m phase transformation. An eventual change of the surface energy through sulfate and phosphate treatment can be sufficient to prevent phase transformation caused by adsorption of water on the surface.

Conclusion

The effect of phosphates and sulfates on the stability of metastable tetragonal zirconia in water and ambient atmosphere at RT was studied. Due to experimental setup—calcination followed by surface treatment with either phosphoric or sulfuric acid—crystal size difference between native and surface treated specimens are neither expected nor observed. Hence retardation of crystal growth cannot be the reason for the observed stabilization. Instead the stabilization of tetragonal zirconia by phosphate and sulfate is caused by anionic interactions with sulfate and phosphate ions on the zirconia surface. The stabilization is either a result of hindered reaction of water on the surface or a result of change in surface energy, which favors the tetragonal phase. Further investigations have to be conducted to understand the stabilizing effect of SO_4^{2-} and PO_4^{3-} ions on tetragonal zirconia at RT.

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References

1. Marcus R, Diebold U, Gonzalez RD (2003) Catal Lett 86:151
2. Reddy BM, Sreekanth PM, Lakshmanan P (2005) J Mol Catal A 237:93
3. Mishra MK, Tyagi B, Jasra RV (2004) J Mol Catal A 223:61
4. Boyse RA, Ko EI (1996) Catal Lett 38:225
5. Segawa K, Kurusu Y, Nakajima Y et al (1985) J Catal 94:491
6. Laginestra A, Patrono P, Berardelli ML et al (1987) J Catal 103:346
7. Garvie RC (1965) J Phys Chem 69:1238
8. Zhang YL, Jin XJ, Rong YH et al (2006) Mater Sci Eng A 438:399
9. Gutzov S, Ponahlo J, Lengauer CL et al (1994) J Am Ceram Soc 77:1649
10. Mekhemer GAH, Ismail HM (2000) Colloids Surf A 164:227
11. Bernstein E, Blanchin MG, Ravellechapuis R et al (1992) J Mater Sci 27:6519. doi:10.1007/BF00576306
12. Skovgaard M, Ahniyaz A, Sørensen BF et al (2010) J Eur Ceram Soc 30:2749
13. Van Lelieveld A, Nielsen MS, Almdal K et al. EP1996144-A2, US2010016465-A1
14. Toraya H, Yoshimura M, Somiya S (1984) J Am Ceram Soc 67:C119
15. Mekhemer GAH (2006) Colloids Surf A 274:211
16. Scherrer P (1918) Goettinger Nachrichten 2:98
17. Sato T, Shimada M (1985) J Am Ceram Soc 68:356
18. Murase Y, Kato E (1979) J Am Ceram Soc 62:527
19. Murase Y, Kato E (1983) J Am Ceram Soc 66:196