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The influence of alcohol additives on the crystallization of ZrO_2 under hydrothermal conditions

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Abstract ZrO_2 small particles with different crystal habits were prepared from zirconium nitrate under hydrothermal conditions. The ZrO_2 particles were characterized by XRD, TEM and SEM. The crystal structure, morphology and size of the ZrO_2 particles were strongly dependent on the glycerin additive in the reaction solution. The phase-pure t-ZrO_2 with the size about 10 nm formed from the reaction solution added with glycerin while the rod-like phase-pure m-ZrO_2 with the size about 30×80 nm formed from the reaction solution without glycerin (180 °C, 18 h, pH = 13). The t-ZrO_2 could also form under the same hydrothermal conditions in the presence of other polyhydric alcohol additives, such as trimethylolpropane and tetramethylolmethane. But monohydric and dihydric alcohols were not benefits to formation of phase-pure t-ZrO_2. The mechanisms for formation of phase-pure t-ZrO_2 were supposed according to the experimental results.

Introduction

Polymorphism is a phenomenon that a substance crystallizes to form several crystals with different structures. ZrO_2 is a classic crystal that has multiple polymorphs. In nature, ZrO_2 has three polymorphs, t-ZrO_2, m-ZrO_2 and c-ZrO_2 [1]. Controlling the ZrO_2 structure is very important not only for scientific research but also for some practical use [2]. For example, in the region of ceramic toughening agent or solid super acidic catalysts, t-ZrO_2 is necessary [3–6]. There are many ways to prepare ZrO_2 particles, but hydrothermal method has attracted more attention in recent years. For hydrothermal reactions offer a number of advantages in contrast to conventional chemical reactions [7–12]. However, the crystalline structure, morphology and particle size of ZrO_2 prepared under hydrothermal conditions are strongly influenced by pH, additives of precursor, time or temperature of reactions, etc. The phase-pure t-ZrO_2 can't form without doping cations, such as Y^{3+}, Ca^{2+}, to the crystal lattice of ZrO_2 [13–15]. There is always m-ZrO_2 existing in the products.

At the present work, alcohol additives were added into reaction solutions. It was found that some alcohol additives evidently influenced on the ZrO_2 crystal structure as well as the particle size and morphology. The phase-pure t-ZrO_2 small particle formed under hydrothermal conditions. The mechanisms for formation of phase-pure t-ZrO_2 were supposed according to the experimental results.

Experimental procedure

Zirconium nitrate ($Zr(NO_3)_4 \cdot 5H_2O$) was used as starting materials to prepared 0.3 mol L^{-1} stock solution. The stock solution turned into transparent after aging for a week. 5.0 mol L^{-1} NaOH aqueous solution

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and de-ionized water were dropwised into 10 mL 0.3 mol L^{-1} stock solutions to form a series of 30 mL reaction solutions with set pH values respectively. To prepare another series of 30 mL reaction solutions with set pH values and alcohol additives, 0.44 mL (0.006 mol) glycerin was added to 10 mL 0.3 mol L^{-1} stock solutions separately, then 5.0 mol L^{-1} NaOH aqueous solution, de-ionized water were dropwised until the total volumes to be 30 mL and the pH to be the set values respectively. The molar ratio of glycerin to zirconium ions was 2:1. So all the zirconium ion concentrations of reaction solutions were 0.1 mol L^{-1}. Hydrothermal reactions were performed in 40 mL stainless steel autoclaves with Teflon liner at 180 °C for designed time. After hydrothermal reactions, the autoclaves were cooled to the room temperature in air. The products were recovered by centrifugal wash and freezing dry (Model 79480, LABCONCO, United States). All the chemical reagents were analytical grade.

ZrO_2 particles were characterized by X-ray powder diffractometer (XRD, Model D8-ADVANCE, Bruker, Germany) with CuKα radiation (0.15406 nm) and graphite monochromator. The XRD patterns were collected in the 2θ range of 20–80°at room temperature. The morphology and particle size of ZrO_2 were observed with transmission electron microscope (TEM, Model JEM-200CX, JEOL, Japan) and environmental scanning electron microscope (ESEM, Model QUANTA200, FEI, The Netherlands).

Results and discussion

Influence of glycerin

Crystalline structure

Phase-pure t-ZrO_2 could not form at any pH value if there was no glycerin in the reaction solution. The results were showed in Fig. 1, which were very similar with Mitsuhashis', who used $ZrOCl_2 \cdot 8H_2O$ as starting materials [16]. However, phase-pure t-ZrO_2 could form when the reaction solution was added with glycerin and pH was greater than 10. But only amorphous ZrO_2 formed when the pH value was less than 10 even there was the glycerin additive in the reaction solution (Fig. 2).

Morphology and size

For the reaction solutions without glycerin additive, when pH value was equal to 13, the rod-like ZrO_2 (about 30 × 80 nm) (Fig. 3) formed after hydrothermal reaction (180 °C, 18 h). As the reaction time was prolonged to 168 h, the rod-like morphology of ZrO_2 was not changed, but the size increased to micro level (about 0.1 × 0.5 μm) (Fig. 4).

The effects of glycerin on the morphology were obvious by comparing Fig. 3 with Fig. 5. Under the same hydrothermal reaction conditions (180 °C, 18 h, pH = 13), small particles (about 10 nm) formed when

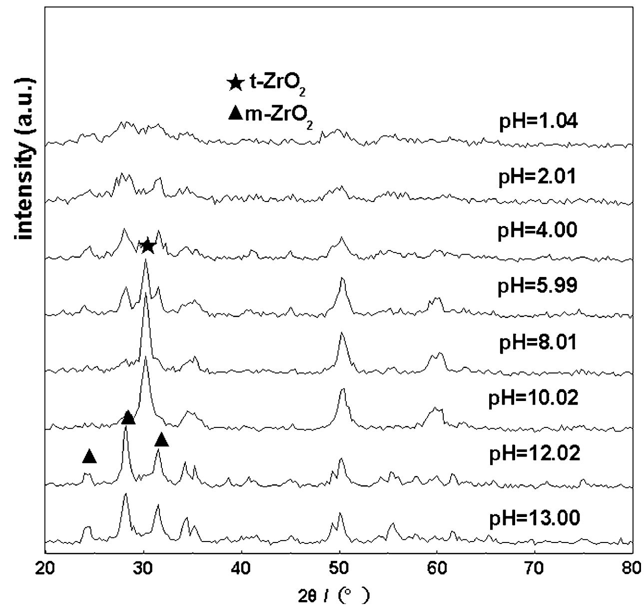

Fig. 1 XRD patterns of ZrO_2 at different pH (180 °C, 18 h)

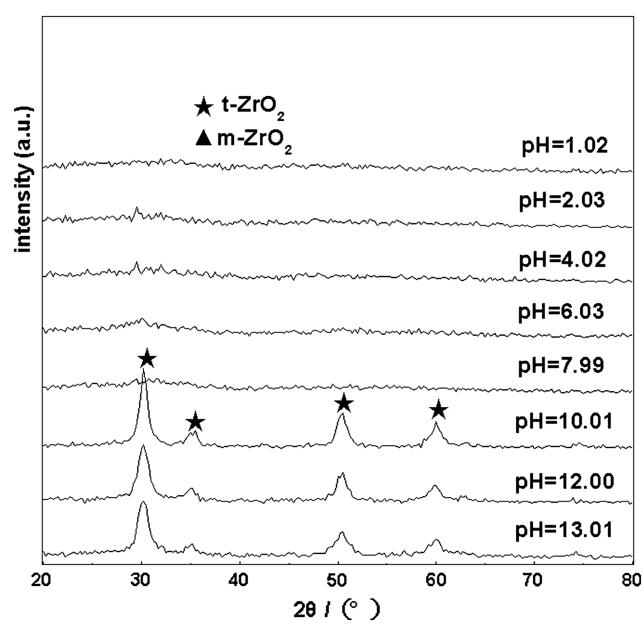

Fig. 2 XRD patterns of ZrO_2 at different pH (with glycerin, 180 °C, 18 h)

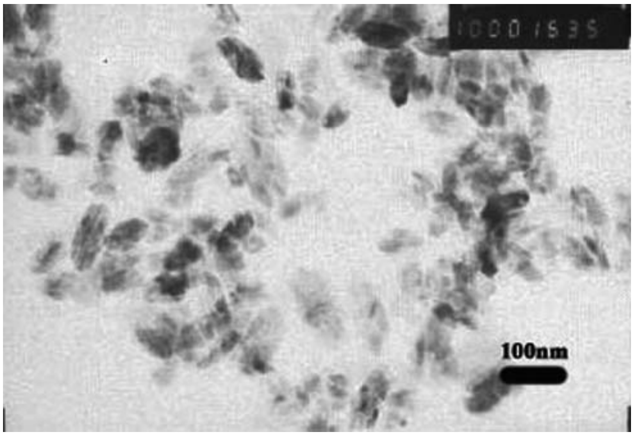

Fig. 3 TEM image of ZrO_2 at pH = 13 (180 °C, 18 h)

the glycerin was added (Fig. 5) while rod-like ZrO_2 (about 30×80 nm) formed without glycerin additive (Fig. 3).

The influence of other alcohol additives on ZrO_2

Other alcohols were also selected as additives for the hydrothermal reaction to investigate the influence of alcohol types on the formation of ZrO_2. Considering the results in section ''Crystalline structure'', the hydrothermal reaction condition was kept at pH = 13, 180 °C, 18 h, because these conditions prefer to form phase-pure t-ZrO_2 when glycerin was added (Fig. 2). The experimental results showed that only m-ZrO_2 formed for monohydric and dihydric alcohol additives, such as ethanol, *n*-propyl alcohol, glycol, 1,2-propylene glycol, 1,3-propylene glycol and butanediol. Otherwise, t-ZrO_2 formed for polyhydric alcohols, such as trimethylolpropane and tetramethylolmethane (Fig. 6).

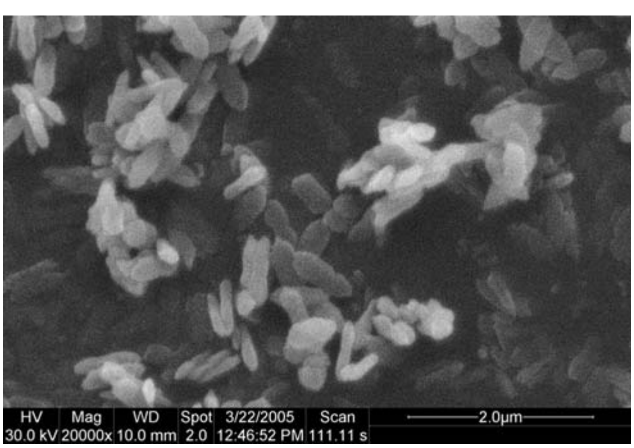

Fig. 4 SEM image of ZrO_2 at pH = 13 (180 °C, 168 h)

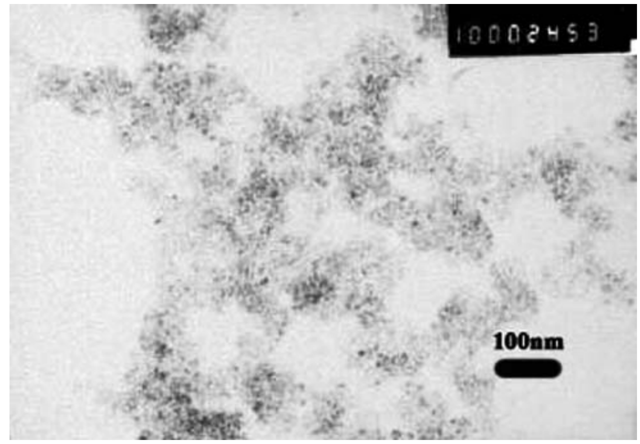

Fig. 5 TEM image of ZrO_2 at pH = 13 (with glycerin, 180 °C, 18 h)

The mechanisms for formation of t-ZrO_2 with glycerin

Transition metal ions M^{z+} are solvated by the surrounding water molecules when they are in aqueous solutions [17]. The aquated ions $[M(OH_2)]^{z+}$, have partial covalent bonds between metal and oxygen atoms. Because of electronegativity of M^{z+}, the follow balance occurs [18]:

$$[M(OH_2)]^{Z+} \leftrightarrow [M\text{–}OH]^{(Z-1)} + H^+ \quad (1)$$

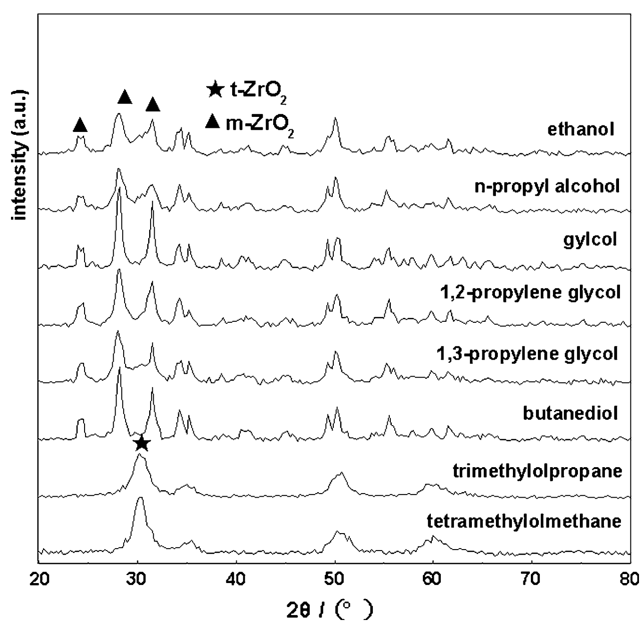

Fig. 6 XRD patterns of ZrO_2 at pH = 13 (with alcohols, 180 °C, 18 h)

When zirconium nitrate was dissolved in water, the zirconium ions form tetramers $[Zr_4(OH)_8(OH_2)_{16}]^{8+}$ by hydrolysis, olation or oxolation. The tetramer has 8 hydroxo bridges and 16 coordinate water molecules (Fig. 7). In strong base conditions, tetramer release hydrogen from the coordinate water:

$$[Zr_4(OH)_8(H_2O)_{16}]^{8+} \leftrightarrow [Zr_4(OH)_{8+x}(H_2O)_{16-x}]^{(8-x)+} + xH^+ \tag{2}$$

Then the group $[Zr_4(OH)_{8+x}(H_2O)_{16-x}]^{(8-x)+}$ has many sites at which condensation takes place and polymeric growth can proceed in many different paths to form oligomers [19–21]. When the concentration of oligomers reaches the critical level, crystal nuclei of ZrO_2 generate and primary particles of ZrO_2 form by growth of the crystal nucleus [22].

It is suggested that if there is glycerin in the reaction solution, water molecules in aquated zirconium ions are replaced by glycerin. As a result, the ways of crystallization are changed to prefer formation of phase-pure t-ZrO_2.

When the pH value of the reaction solution was less than 10, amorphous ZrO_2 formed, which means crystallization process of ZrO_2 was inhibited (Fig. 2). From the Eq. 1, it can be deduced that hydrolysis of zirconium ions was restrained at low pH conditions, so the concentration of oligomers with hydroxyl groups could not reach the critical level and form ZrO_2 crystal nuclei. Even the ZrO_2 crystal nuclei formed, glycerin molecules probably adsorbed to the ZrO_2 crystal nuclei leading to inhibit crystallization process.

When pH of the reaction solution was greater than 10, hydrolysis occurs easily. The concentration of oligomers could reach the critical level and form crystal nuclei. On the other hand, the glycerin molecules existed in the reaction solution probably adsorbed to the fresh crystals and the crystal growth was reduced because of lacking growth sites. That was the reason why the ZrO_2 particles formed with the glycerin additive was much smaller (about 10 nm) than the size of ZrO_2 (about 30 × 80 nm) formed without glycerin additive (Figs. 3, 5).

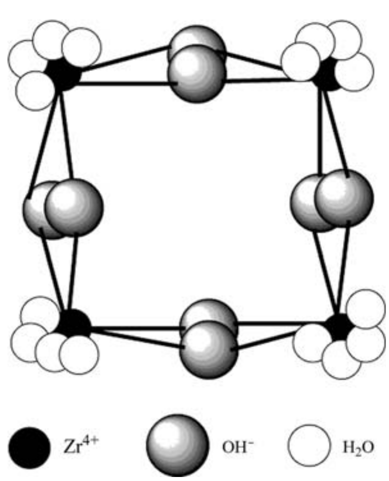

Fig. 7 The structure of $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$

It was supposed that polyhydric alcohols (e.g. glycerin) in reaction solution have strong interaction with zirconium ions in this experimental condition than monohydric and dihydric alcohols for polyhydric alcohols have more hydroxyl groups. Especially, 1,2-propylene glycol and 1,3-propylene glycol, which are very similar with glycerin in structure, were not benefit to formation of phase-pure t-ZrO_2. It was indicated that the number of hydroxyl groups was the key factor for the formation of t-ZrO_2 under this experimental condition. For polyhydric alcohols, one molecule probably supplies two or more hydroxyl groups to chelate with zirconium ions. The chelating products of polyhydric alcohols and zirconium ions could be more suitable to form t-ZrO_2 perhaps for the reasons of the space structure or active energy of the chelating products. For monohydric or dihydric alcohols, having only one or two hydroxyl groups per molecule, they have less chance to form chelating products with zirconium ions (Fig. 6).

Indeed, further experiments should be conducted to find the detail reasons for the different influences of alcohol types.

Conclusions

ZrO_2 small particles can be prepared from Zirconium nitrate ($Zr(NO_3)_4 \cdot 5H_2O$) under hydrothermal conditions. The crystalline structure, morphology and particle size of ZrO_2 was strongly dependent on pH value and the types of alcohol additives.

1. In the presence of glycerin additive in the hydrothermal reaction solution, amorphous ZrO_2 formed if pH value of the reaction solution was less than 10 or pure-phase t-ZrO_2 formed if the pH value of reaction solution was greater than 10 after hydrothermal reactions.
2. t-ZrO_2 small particles (about 10 nm) formed after hydrothermal reactions (180 °C, 18 h, pH = 13) if there was glycerin additive in the reaction solution. While rod-like ZrO_2 particles (about 30 × 80 nm) formed under the same hydrothermal conditions if there was no glycerin additive in the reaction solution.

3. Polyhydric alcohols such as trimethylolpropane and tetramethylolmethane can also be taken as additives for the formation of pure-phase t-ZrO_2 under the hydrothermal condition (180 °C, 18 h, pH = 13). But monohydric and dihydric alcohol such as ethanol, *n*-propyl alcohol, glycol, 1,2-propylene glycol, 1,3-propylene glycol and butane-diol can be taken as additives for the formation of m-ZrO_2.

References

1. Yanqing Z, Erwei S et al (2002) Sci China (Ser. E) 45(4):273
2. Laverne JA (2005) J Phys Chem B 109(12):5395
3. Garvie RC (1975) Nature 258:703
4. Kim B-N, Hiraga K et al (2001) Nature 413:288
5. Ma Z-Y, Yang C et al (2005) J Mol Catal A-Chem 227:119
6. Morterra C, Cerrato G et al (2002) Phys Chem Chem Phys 4:3136
7. Rabenau A (1985) Angew Chem Int Ed Engl 24:1026
8. Piticescu RR, Monty C et al (2001) J Eur Ceram Soc 21:2057
9. Yoshimura M et al (1999) Mater Chem Phys 61:1
10. Dell' Agli G, Mascolo G (2000) J Mat Sci 35:661
11. Stefanic G, Popovic S et al (1997) Thermochim Acta 303:31
12. Jiao X, Chen D et al (2003) J Cryst Growth 258:158
13. Dell' Agli G et al (1999) Solid State Ionics 123:87
14. Hu-Min C et al (1999) J Eur Ceram Soc 19:1675
15. Xu G, Zhang Y-W et al (2004) J Am Ceram Soc 87(12):2275
16. Mitsuhashi T, Ichihara M et al (1974) J Am Ceram Soc 57:97
17. Tingyao S (1990) In: Coordination chemistry. Chendu University of Science and Technology Press, SiChuan, China, p 34
18. Bokhimi X, Morales A et al (1999) Nanostruct Mater 12:589
19. Livage J (1998) Catal Today 41:3
20. Toth LM, Lin JS, Felker LK (1991) J Phys Chem 95:3106
21. Singhal A, Toth LM et al (1996) J Am Chem Soc 118:11529
22. Matsui K, Ohgai M (2001) J Am Ceram Soc 84(10):2303