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Stabilization of mesoporous nanocrystalline zirconia with Laponite

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Abstract **The mesoporous nanocrystalline zircoina was synthesized via solid state reaction——structure directing method in the presence of Laponite. The introduction of Laponite renders the higher thermal stability and lamellar track to the zirconia. Laponite acts as inhibitor for crystal growth and also hard template for the mesostructure. The role of Laponite is attributed to the interaction between the zirconia precursors and the nano-platelets of Laponite via the bridge of hydrophilic segments of surfactant. It results in the formation of Zr-O-Mg-O-Si frameworks in the direction of Laponite layer with the condensation of frameworks during the calcination process, which contributes the higher stability and lamellar structure to the nano-sized zirconia samples.**

Keywords: mesoporous nanocrystalline zirconia, Laponite, stabilization mechanism.

ZrO_2 has attracted much attention because of its high performance as structural materials, electrode materials, electronics and oxygen sensors, supports and catalysts[1—6]. However, a major problem of this nonsiliceous oxide is its thermal stability. The surfactant removal by calcination, as used for porous silicates, leads to structure collapse because of phase transformation, hydrolysis and redox reaction occurring at elevated temperature, which results in the loss of surface area and porosity. In addition, nano-sized particles prefer to aggregate to resist its higher surface energy. It means that for mesostructured or nanocrystalline zirconia, thermal stability is always a challenging area.

Recently, many synthesis routes have been proposed for the synthesis of thermally stable zirconia. The major approaches are to tune its electronic property or to enlarge the pore wall[7—11]. For example, the inorganic framework is either phosphate or sulfate groups as stabilizers[12—14]. These anions can inhibit the crystallization of precursor species during the calcination. The introduction of phosphate or sulfate groups can be achieved by the self-assembly process of organic and inorganic species using the surfactant with phosphate or sulfate hydrophilic head or by post treatment with these anions after the materials are obtained. Also, aliovalent and tetravalent dopants, such as Na^+, Ca^{2+}, Y^{3+}, Si^{4+}, Ce^4, Th^{4+}, etc. have been used to reinforce the nanocrystalline structures[15—19]. The stabilization was believed to be achieved by strong surface interaction between dopants ions and zirconia or by higher coordination number via addition of large size dopants.

The zirconia prepared via solid-state reaction——structure directing method——bear large surface area and optimum pore structure[20]. Its phase can be tailored among amorphous, tetragonal and monoclinic phase by controlling the synthesis parameters. In order to improve the thermal stability of the zirconia with MSU structure, Laponite was introduced into the inorganic framework. This study demonstrates that electronic and structural effects of Laponite render good stability to zirconia.

1 Experimental

(ⅰ) Sample preparation. The approach to synthesizing the mesoporous nanocrystalline zirconia is the same as that of ref. [20]. The stabilization of framework was also solid-state reaction. In a typical synthesis, a certain amount of Laponite was milled together with zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$), and then PEO-block-PPO surfactant (F.W. = 5800) was introduced into the above mixture by vigorously stirring. After that, the mixture reacted with milled sodium hydroxide whose amount is quarter mole of zirconyl chloride. The product was then transferred into an autoclave and kept at a 383 K for 48 h. Subsequently, the sample was washed with deionized water until it was free of Cl^- ions, and then washed with ethanol twice to remove water and surfactant contained in the solid. Finally, the samples were dried at 383 K overnight.

(ⅱ) Characterization. Nitrogen adsorption and desorption isotherms at 77.3 K were carried out with Autosorb-1C (Quantachrome, USA) after degassing at 200℃ for 10 h. The mesopore size distribution was calculated from the desorption branch of the isotherms. X-ray powder diffraction (XRD) patterns were obtained with a Bruker Axs (Germany) diffractometer, using Co Kα radiation with a tube voltage of 40 KV, and a tube current of 20 mA. Transmission electron microscopic (TEM) images were taken using a Philips CM200 Microscope in bright field transmission model. The samples for TEM were prepared by directly dispersing the zirconia particles treated by ultrasonic dispersion onto holey carbon grids. Energy-disperse X-ray (EDX) spectra were taken on a Gatan detector connected to the electron microscope.

2 Results and discussion

The data in Table 1 and Fig. 1 demonstrate that Laponite is a good stabilizer for zirconia. When incorporat-

ing 7% mass ratio of Laponite into the synthesis, the surface area and pore diameter of the sample calcined at 450℃ can be comparable with as-made product. The BET surface area is still up to 231.2 m^2 · g^{-1} even calcined at 600℃ for 20 h. It is worthywhile to note that the pore structure can be almost retained at this high elevated temperature. Fig. 1 shows that the pore diameter of pure zirconia is distinctly enlarged with an increase in calcination temperature; otherwise, it is nearly duplicated for the stabilized samples calcined at any investigated temperature. Moreover, in the presence of Laponite, the mesoporous system is more developed and pore distribution tends to be narrower. It means that the incorporation of Laponite to the inorganic framework can resist the expanding of pore mouth, thus rendering higher surface area to the zirconia.

Table 1   Role of Laponite to the surface area and pore structure of zirconia

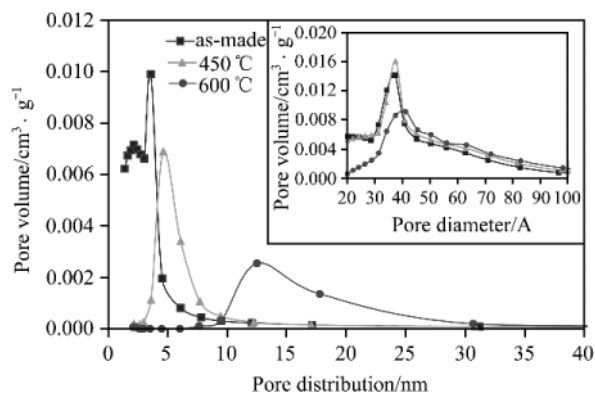| Sample	BET/m^2.g^{-1}	Pore volume /cm^3.g^{-1}	Pore diameter /nm
As-made	397.2	0.412	4.61
450℃	103.3	0.279	6.12
600℃	40.0	0.267	17.80
As-made	356.5	0.454	4.08
450℃	360.9	0.472	4.10
600℃	231.2	0.411	4.56

Fig. 1.   Mesopore size distribution of zirconia calcined at different temperatures. Inset: pore size distribution of samples stabilized by Laponite.

XRD studies on samples indicate that nanocrystalline zirconia can be synthesized via this novel method and crystallization can occur during the calcination. The diffraction peaks of calcined stabilized sample shown in Fig. 2 are more broadened than the as-made pure zirconia. This means that Laponite must have been incorporated into the zirconia framework and there formed a strong interaction with Zr^{4+}. The intimate interaction between zirconia precursors and inorganic species of the Laponite is so strong that Zr-O-Mg-O-Si network may be formed at elevated temperature. This network inhibits the crystal growth during calcination, and consequently there form more fine

nanocrystallites. In addition, Si, Mg species also act as the barriers for the Zr species, resisting the aggregation of nanosized zirconia particles. This proposal is further confirmed by TEM images.
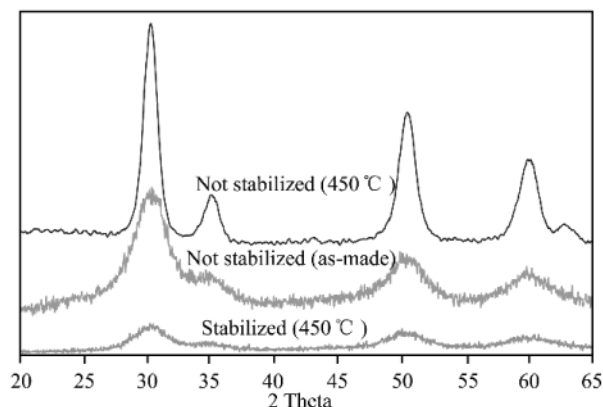

Fig. 2.   XRD pattern of calcined zirconia before and after stabilization.

TEM images in Fig. 3 show that all the samples bear MSU structure and nanosized particles. Selected-area electron diffraction patterns indicate that the pore walls of zirconia are made up of nanocrystalline with characteristic diffuse electron diffraction rings. This crystalline structure effectively sustains the local strain caused by the crystallization and prevents the mesostructure from collapsing, which contributes good thermal stability to the samples[10,11]. The particle size of the sample stabilized with Laponite is much smaller than pure zircona. This phenomenon is prominent for calcined samples. The size of zirconia modified with 7% mass ratio of Laponite and calcined at 600℃ is only 2.0 nm or so. It can be compared with the as-made sample. For pure zirconia, it is increased from 1.5nm of as-made sample to 6.0—7.0 nm of sample calcined at 450℃. This result is consistent with the XRD diffraction lines. The mesoporous structure and lattice finger of pure zirconia calcined at 450℃ are apparently exhibited in Fig. 3(c). The pore diameter is about 6.2 nm, which corresponds to the value of 6.1 nm calculated by BJH method.

Interestingly, the mesostructure of Laponite stabilized samples looks more ordered than that in the pure zirconia. The local lamellar structure can be observed in the mesostructure of the calcined sample. It indicates that Laponite can act as hard template during the mesostructure formation. Its templating is achieved by the synergy with soft template (surfactant). In the solid-state synthesis, the precursor of zirconia and inorganic species in Laponite can interact via hydrogen boning between the PEO segments of surfactant and various inorganic species. This interaction may be extended in the direction of Laponite platelet layer. The Zr-O-Mg-O-Si network is formed upon
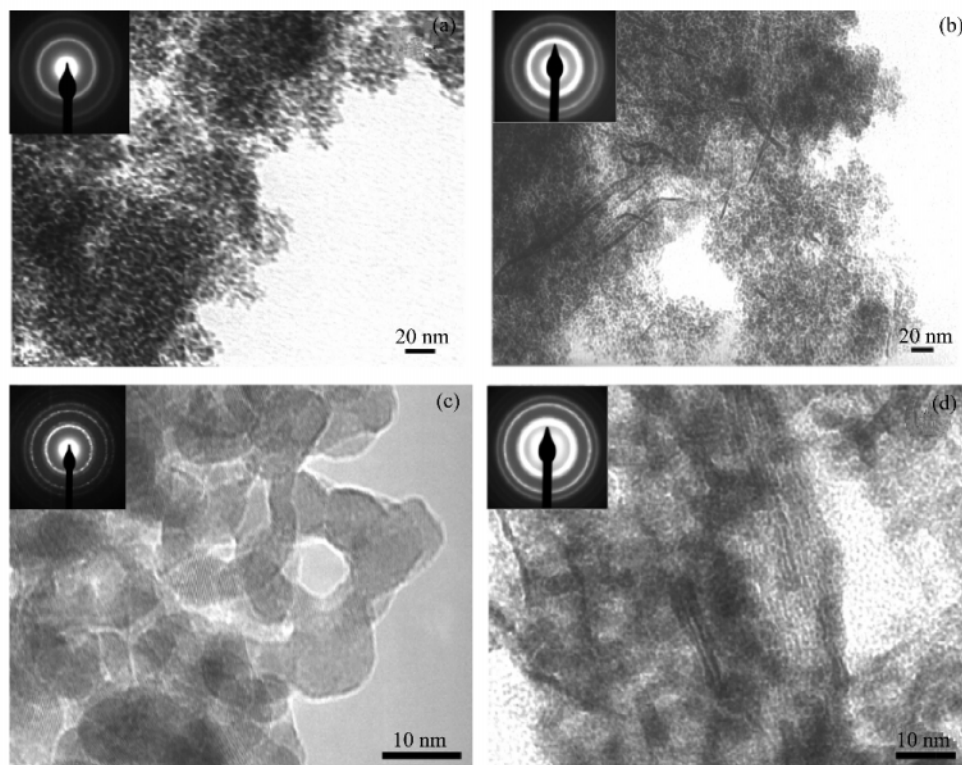
Fig. 3.   TEM images of pure and stabilized zirconia before and after calcination. (a) As-made pure zirconia; (b) zirconia stabilized by 7% Laponite; (c) pure zirconia calcined at 450℃; (d) zironia stabilized with 7% Laponite and calcined at 600℃.

condensation of inorganic pore wall at high temperature. That is why the mesostructure of calcined Laponite stabilized sample is more ordered.

The stabilization mechanism of Laponite to the zirconia is illustrated in Fig. 4. In the solid-state synthesis system, zirconia chloride, Laponite and surfactant are sufficiently mixed first, and then react with NaOH. Subsequently, the product is crystallized in autoclave. In the crystallization, the hydrogen bonding is formed between hydrophilic segments and precursor of zirconia, simultaneously, formed between hydrophilic segments and Si or/and Mg species in Laponite layer. However, these weaken hydrogen bonding transform to M-O bond with the condensation of skeleton hydroxyl at higher temperature, which contributes to the connection among various inorganic species via oxygen atoms. Let it be noted here that the interaction among various inorganic species can be extended in the direction of Laponite platelet layer. This is why local lamellar structures can be observed in the zirconia mesostructure. The Zr-O-Mg-O-Si networks with large covalent bonds induce stronger interaction for the framework.   It is believed that the introduction of Laponite not only renders the lamellar structure but also form the solid mesoporous skeleton. It is the large covalent bonds network that contributes the higher stability to the mesostructure.

N_2 adsorption/desorption isotherms showing IV or V type with hysteresis loop are obtained for the zirconia modified with different amounts of Laponite, which further confirmed that zirconia prepared with solid-state reaction─structure directing method are representative of mesoporous materials. The more introduction of Laponite into the framework, the larger of hysteresis loop is observed as shown in Fig. 5. The change of hysteresis loop is believed to be related to the pore structure. The mesopore size tends to be larger and pore distribution is broadened. The Barrett-Joyner-Halenda (BJH) analyses in Fig. 5(b) show that the zirconia stabilized with above 7% mass ratio of Laponite exhibit bimodal distribution, and pore size can be up to 10 nm. While for sample prepared with lower than 7% ratio, there is just one narrow peak, and pore is concentrated on 4.1nm. The change of pore structure is attributed to the modification of mesostructure with amount of addition of Laponite. The local lamellar structure can be extended to long distance with zirconia precursors incorporated into more Laponite layers. The connection of Zr-O-Si-O-Mg network renders larger mesopore to the samples. Simultaneously, the pore volume is increased and surface area reaches maximum value with Laponite introduction. All these results are listed in Table 2.

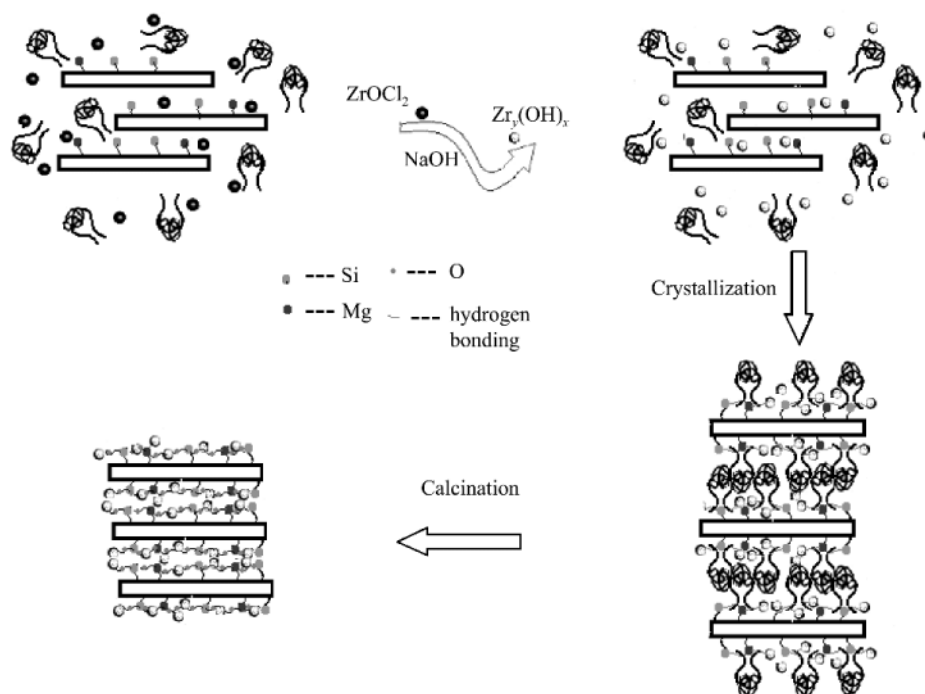The data in Table 2 also show that the particle size of

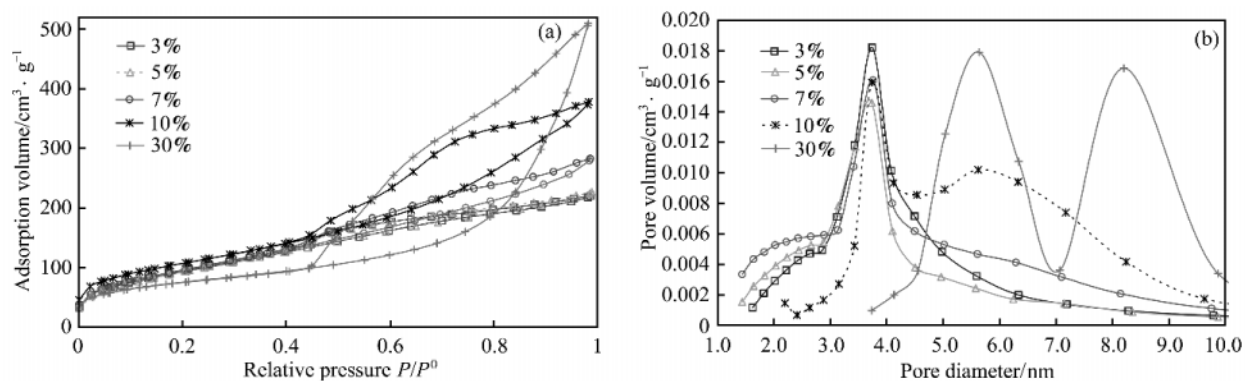Fig. 4.   Schematic of stabilization mechanism of Laponite to the zirconia.

Fig. 5.   Surface area and pore structure of stabilized zirconia with increase of Laponite (mass ratio to $ZrOCl_2 \cdot 8H_2O$).

Table 2   The effect of introduction amount of Laponite on physical properties of zirconia

Sample	Particle size /nm	BET /m²·g⁻¹	Pore volume /cm³·g⁻¹	Pore diameter/nm
Zr-Lap-3	2.7	287.9	0.383	4.08
Zr-Lap-5	2.1	282.2	0.334	4.10
Zr-Lap-7	2.0	360.9	0.472	4.10
Zr-Lap-10	1.8	309.7	0.582	4.12, 5.80
Zr-Lap-30	1.5	276.2	0.914	6.34, 9.87

The number in sample name is depicted as the mass ratio of laponite to the $ZrOCl_2 \cdot 8H_2O$.

stabilized zirconia is decreased with the increase of Laponite introduction. This can be demonstrated from XRD patterns showing weakened intensity (Fig. 6). The asym-
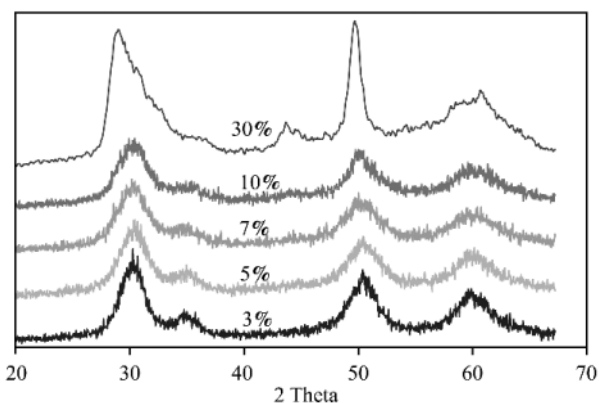

Fig. 6.   Effect of introduction of Laponite on the XRD patterns of zirconia.

metry peak of sample prepared with high presence of Laponite indicates the transformation of mesostructure.

3 Conclusion

The results demonstrate that Laponite acted as inhibitor of nano-sized zirconia agglomeration and hard template for the ordered mesostructure formation. It not only improves the thermal stability but also positively render the more ordered mesoporous structure. Under the synthesis condition, the zirconia precursors intimately interact with the nano-platelets of Laponite via the bridge of hydrophilic segments with hydrogen bond and the Zr-O-Mg-O-Si frameworks were formed in the direction of Laponite layer with the condensation of frameworks during the calcination process. It is the formation of Zr-O-Mg-O-Si network that resists the crystallization of zirconia precursor and renders local lamellar structure to the nanocrystalline zirconia.

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