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Synthesis of mesoporous nanocrystalline zirconia with tetragonal crystallite phase by using ethylene diamine as precipitation agent

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Abstract Mesoporous nanocrystalline zirconia with high surface area and pure tetragonal crystallite phase has been prepared by bifunctional ethylene diamine as both precipitating agent for $ZrO(NO_3)_2$ to $ZrO(OH)_2$ and colloidal protecting agent for the $ZrO(OH)_2$ nanoparticles. The effect of refluxing time and temperature on the structural properties of the zirconia were investigated. The obtained results showed that the increasing in refluxing time and temperature improved the thermal stability and increased the tetragonal content of the zirconia. The results also showed that the addition of Pluronic P123 block copolymer surfactant acted as a cosurfactant and increased the specific surface area of the zirconia.

Introduction

Zirconia is an important material because of its use in different areas of chemistry such as in ceramics and catalysis. Its catalytic properties are especially promising because zirconia has both acidic and basic properties as well as a high thermal stability. For a number of reactions, zirconia is used as a catalyst support because higher activity and selectivity can be obtained. The use of zirconia requires a high specific surface area and suitable pore structure for catalysis applications. Of interest is the unique properties of nanoparticles make them of interest for catalysis applications. Many researchers have tried to prepare nanostructured zirconia with high surface area with various methods, such as: sol–gel process [1], reverse micelle method [2], coprecipitation [3, 4], hydrothermal synthesis [5], functionalization of oxide nanoparticles and their self-assembly [6] and templating [7], etc. Recently, the surfactant-assisted synthesis of nanoinorganic materials has attracted considerable interest because of its effective soft template effect, reproducibility and simple maneuverability. Using a cationic surfactant, Trens et al. [7] synthesized mesoporous zirconia with high surface area. Using block-copolymer templating, Yang and co-workers [8] demonstrated that the mesoporous zirconia could be synthesized in nonaqueous solution. In this paper, the synthesis of mesoporous nanocrystalline zirconia with bifunctional ethylene diamine as both precipitating and colloidal protecting agent has been investigated.

Experimental

Materials

The starting materials were $ZrO(NO_3)_2 \cdot xH_2O$ (x ca. 6) as zirconium precursor and ethylene diamine as both precipitating as well as colloidal protecting agent. The Pluronic P123 block copolymer was used as a cosurfactant.

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Zirconia preparation

In a typical preparation, ethylene diamine was added dropwise at room temperature to an aqueous solution containing zirconium precursor (0.03 M) under rapid stirring with careful control of pH 11. After precipitation, the slurry was stirred for another 30 min and then refluxed at different temperatures for a certain time under continuous stirring. The mixture then was cooled to room temperature, filtered and washed, first with de-ionized water and finally with acetone. The final product was dried at 110 °C for 24 h and calcined at 600 °C for 4 h. A diagram of the preparation steps is shown in Fig. 1.

Characterization

The surface areas (BET) were determined by nitrogen adsorption at –196 °C using an automated gas adsorption analyzer (The Tristar 3000, Micromeritics). The pore size distribution was calculated from the desorption branch of the isotherm by the Barrett, Joyner and Halenda (BJH) method. The XRD patterns were recorded on an X-ray diffractometer (PANalytical X'Pert-Pro) using a Cu Kα monochromatized radiation source and a Ni filter in the range 2θ = 10–80°. The relative amounts of tetragonal and monoclinic ZrO_2 present in samples and the crystallite sizes were estimated as described elsewhere [9]. Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out in a Netzsch STA 409 system in a static air atmosphere at a heating rate of 10 °C/min. Infrared spectra were recorded on a NEXus Fourier transform infrared (FT-IR) spectrophotometer using KBr pellets containing 1% weight sample in KBr. TEM investigation was performed with Philips CM200 FEG UltraTwin operated at 200 kV.

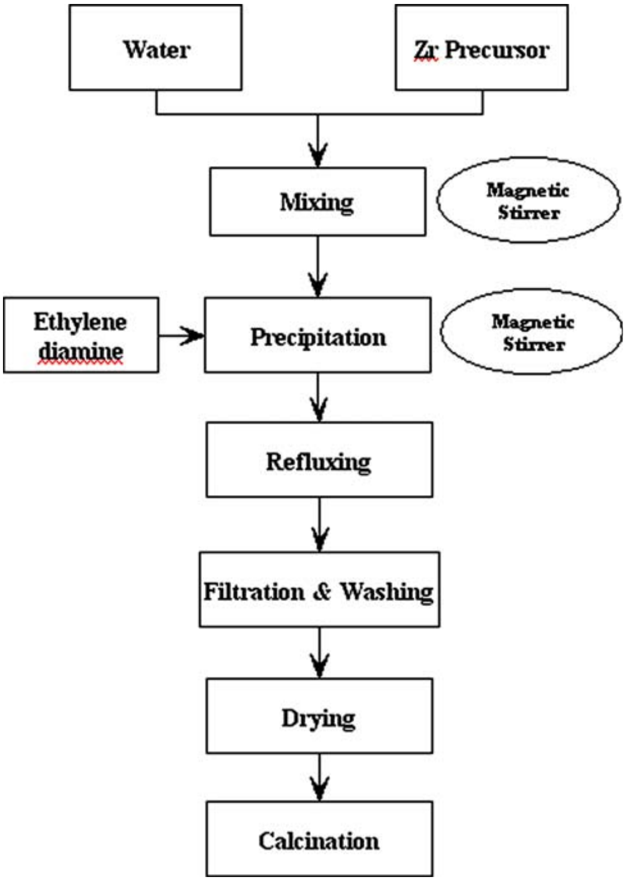

Fig. 1 The preparation of zirconium oxide

Results and discussion

FT-IR and TGA/DTA analyses

Figure 2 shows the IR spectra of the sample after washing steps and calcination at 600 °C for 4 h. As it can be seen, the intensity of the symmetry stretching 2,920 cm^{-1} and asymmetry stretching 2,850 cm^{-1} mode of the CH_2 groups of the ethylene diamine is weak after washing steps, indicating that there is still some ethylene diamine in the pores. However, the peaks arising from the ethylene diamine completely disappear after calcination at 600 °C for 4 h.

The TGA and DTA curves of this sample are shown in Fig. 3. The DTA curve presents three major peaks; in which, two are endothermic and the other is exothermic. The first and second endothermic peaks appear at around 100 and 210 °C, respectively, which corresponds to the elimination of residual water.

The third endothermic peak at about 380 °C could be due to the elimination of the hydroxyl group bonded on the

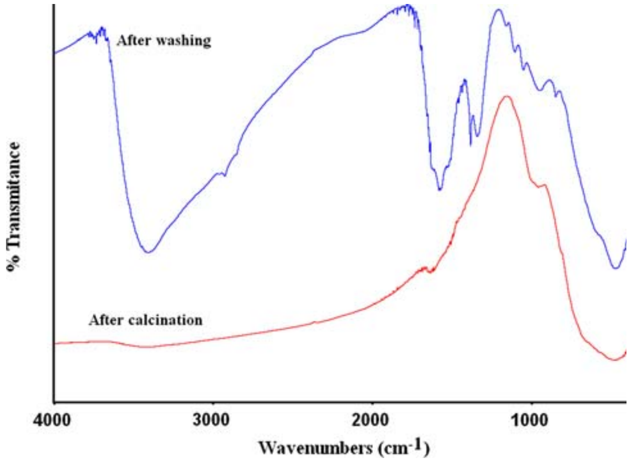

Fig. 2 The FT-IR spectra of the zirconia sample, refluxing time: 24 h, refluxing temperature: 80 °C

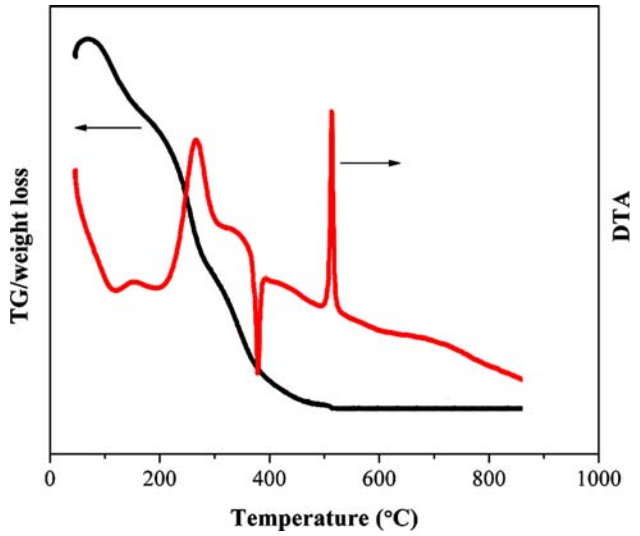

Fig. 3 DTA/TGA curves of the sample, pH 11, refluxing time: 24 h, refluxing temperature: 80 °C

surface of zirconia. The exothermic peak at about 515 °C, usually called ''glow exotherm'', is attributed to the crystallization of amorphous zirconia. Simultaneously, the TG curve is leveled off at about 500 °C, meaning that the organic residues have been removed completely and it also confirmed the FT-IR results.

Effect of refluxing temperature

The pore size distributions of the samples prepared under different refluxing temperatures are shown in Fig. 4a. It is seen that all the samples showed porous structure, although the porosity was very low under the synthesized conditions. The pore size distribution of the samples showed that some mesoporosity were formed. The obtained results also indicated that the increasing in refluxing temperature increased the mesoporosity.

The BET measurements, Table 1, showed that the specific surface area increases by increasing the refluxing time and a material obtained with higher thermal stability.

The nitrogen isotherms, Fig. 4b, can be classified as a type IV isotherm, typical of mesoporous materials. According to IUPAC classification, the hysteresis loop is type H2 indicating a complex mesoporous structure. This type of hysteresis is characteristic of solids consisting of particles crossed by nearly channels consolidated by aggregates or agglomerates. Increasing refluxing times did not alter the hysteresis shape, indicating that pore shape has been maintained after the refluxing process.

Figure 5 shows the XRD patterns of the samples prepared at different refluxing temperatures. The XRD patterns indicated that crystallite phase of the samples was a mixture of monoclinic and tetragonal phase. The obtained results showed that the increasing in refluxing temperature increased the tetragonal content. The sample with the highest refluxing temperature showed the highest tetragonal content. Of interest is that the tetragonal phase was stabilized at room temperature without addition of any dopants. The thermodynamically most stable ZrO_2 phase at room temperature is the monoclinic phase (m-phase). Probably, the nano-size effect of the ZrO_2 crystallites leads to the thermal stabilization of tetragonal phase (t-phase) [10, 11]. Garvie suggested that difference in the surface energy between the tetragonal and monoclinic phases could cause the tetragonal phase to be thermodynamically stable for very small crystals [11, 12]. The crystallite size of the samples, determined by Scherrer equation revealed that the increasing in refluxing temperature decreased the tetragonal cryatallite size, Table 1.

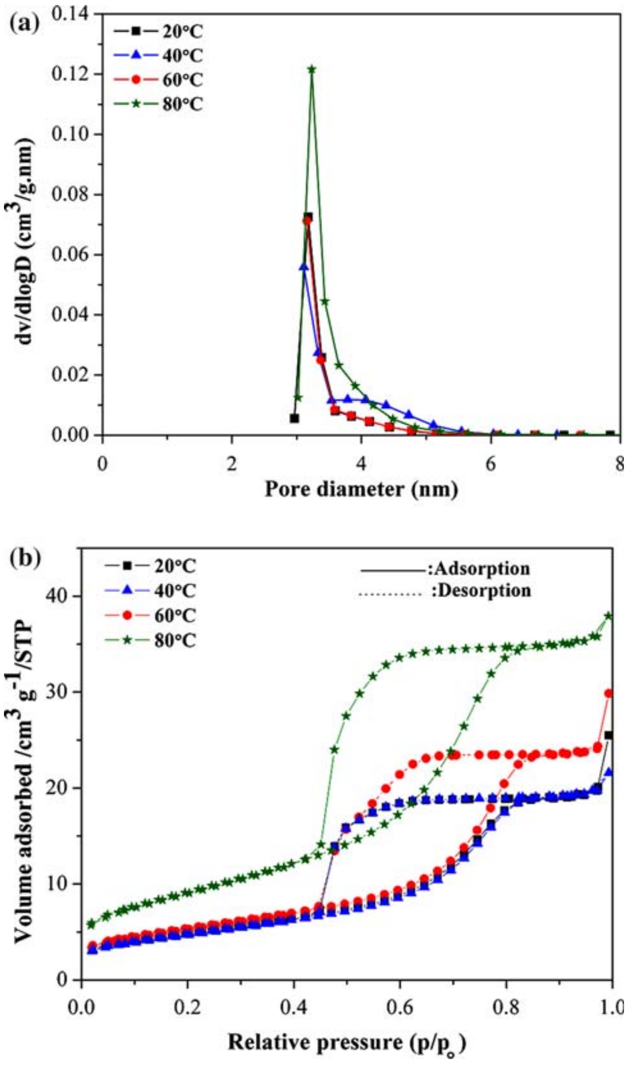

Fig. 4 Effect of refluxing temperature on the (**a**) pore size distributions and (**b**) N_2 adsorption/desorption isotherms, refluxing time: 24 h

Table 1 Effect of refluxing temperature on the structural properties of the samples, refluxing time: 6 h

Reflux temp. (°C)	BET area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Pore diameter (nm)	t_{phase} (wt%)	Crystalline size (nm)		
					$m(\bar{1}11)$	m(111)	t(101)
20	17.6	0.04	4.51	55	14.1	16.5	22.2
40	19.4	0.05	4.51	67	14.1	17.2	22.9
60	17.4	0.03	3.81	68	14.4	23.6	20.5
80	33.4	0.06	3.78	78	25.6	n.d.	16.8

Effect of refluxing time

Figure 6 shows the pore size distributions and nitrogen adsorption/desorption isotherms of the samples prepared under the different refluxing times. It is seen that all the samples showed a mesoporous structure with a narrow pore size distribution between 2 and 5 nm. The N_2 adsorption–desorption isotherm indicate a type IV isotherm with a H2 hysteresis loop. As it was described before, this type of hysteresis is associated with capillary condensation in mesopores and a limiting uptake over a range of high P/P_0. The H2 loop indicates that the pores are of ink bottle shape.

The BET measurements showed an increase in specific surface area with increasing in refluxing time, Table 2.

Figure 7 shows the TEM analysis of the zirconia sample prepared at refluxing time and refluxing temperature of 80 °C and 24 h, respectively. As it can be seen, this sample did not show an ordered mesoporous structure, although the pore size distribution and N_2 adsorption/desorption isotherm suggested the formation of certain mesoporosity. The TEM analysis showed that the particles are sintered together and most of the particles have a slightly irregular, rounded shape.

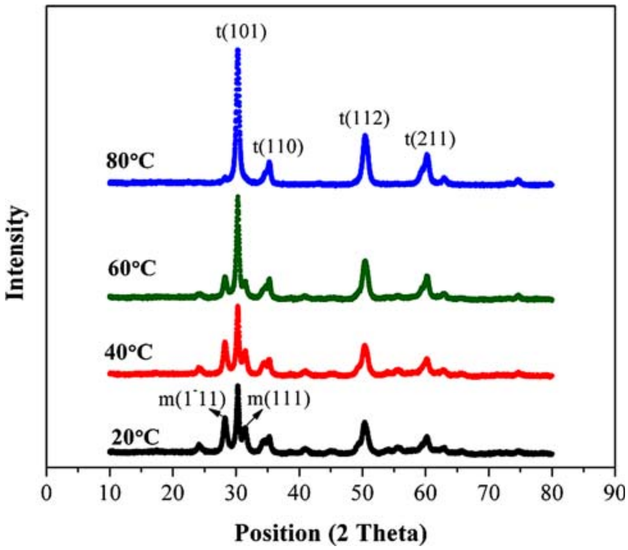

Fig. 5 XRD patterns of the samples prepared at different refluxing temperatures, refluxing time: 6 h

Figure 8 shows the XRD patterns of the samples prepared under different refluxing times. The XRD patterns indicated that the tetragonal phase was the major crystallite phase. The XRD results showed a complete transformation of monoclinic to tetragonal phase at refluxing times longer than 6 h. Of especial is the intensity of the peak, corresponding to t(101) was decreased by increasing in refluxing time, which means a decrease in tetragonal crystallite size by increasing in refluxing time.

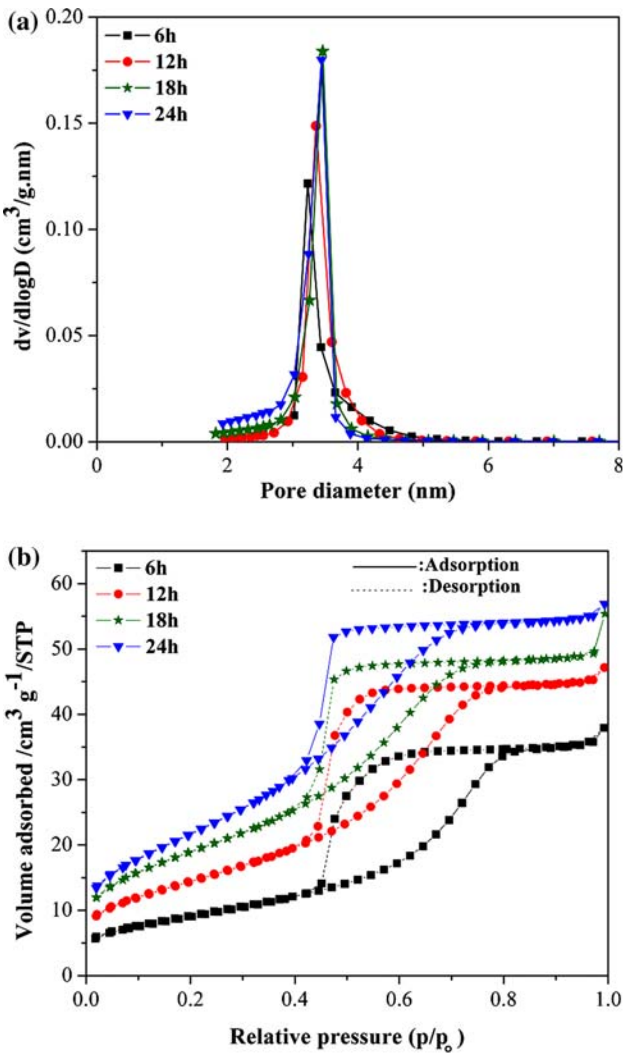

Fig. 6 Effect of refluxing time on the (**a**) pore size distributions and (**b**) N_2 adsorption/desorption isotherms, refluxing temperature: 80 °C

Table 2 Effect of refluxing time on the structural properties of the samples, refluxing temperature: 80 °C

Reflux time (h)	BET area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Pore diameter (nm)	t_{phase} (wt%)	Crystalline size (nm)				
					m($\bar{1}$11)	m(111)	t(101)	t(110)	t(112)
6	33.4	0.06	3.78	78	25.6	n.d.	16.8	13.2	9.4
12	53.2	0.07	3.61	100	–	–	13.7	9.9	9.1
18	69.1	0.09	3.56	100	–	–	14.4	10.3	8.6
24	80.9	0.09	3.33	100	–	–	11.6	9.3	8.2

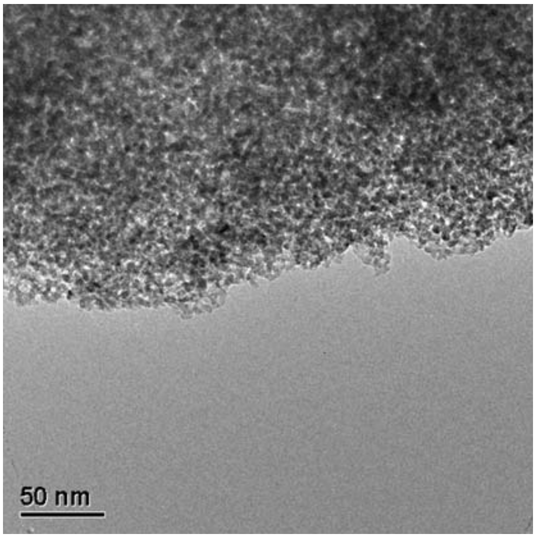

Fig. 7 TEM analysis of the Zirconia sample, refluxing temperature: 80 °C, refluxing time: 24 h

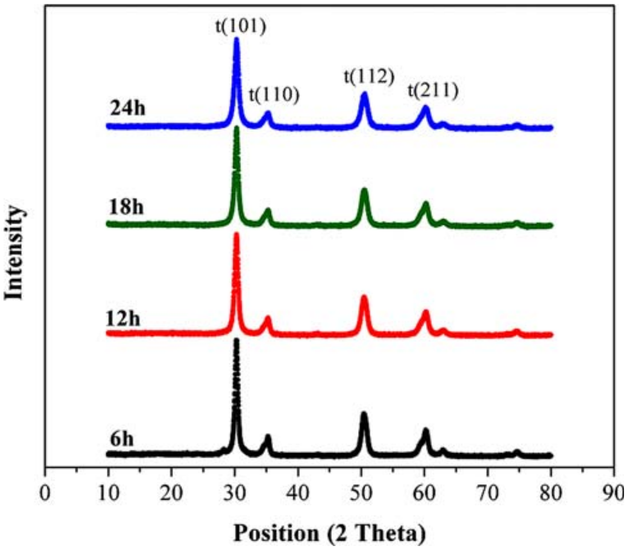

Fig. 8 XRD patterns of the samples prepared at different refluxing times, refluxing temperature: 80 °C

A DTA measurement, Fig. 9, was performed to check the possible influence of the refluxing time on the crystallization temperature. The strong exotherm appearing in DTA curves of zirconia is due to the crystallization, as stated before. It clearly shows that the increasing the refluxing time the crystallization temperature of zirconia increased, as the glow peak of zirconia was observed at higher temperature with increasing in refluxing temperature.

The increase in crystallization temperature could be explained by the effect of refluxing temperature on the crystallite size of the zirconia. As the XRD results (Table 2) showed, increasing in refluxing time decreased the crystallite size of the zirconia and increased the specific surface area, which could increase the crystallization temperature.

Effect of P123 on the structural properties of the zirconia

Figure 10 shows the XRD patterns of the zirconia samples prepared by addition of Pluronic P123 block copolymer as cosurfactant for ethylene diamnie. As it can be seen, the intensity of the peak, corresponding to t(101) was decreased by addition of P123 block copolymer. Table 3 shows the structural properties of the samples. The obtained results showed a decrease in the crystallite size of the tetragonal phase with increasing in P123/Zr molar ratio. The smallest crystallite size was observed for the samples prepared by a P123/Zr ratio of 0.07.

The pore size distributions of the samples prepared by different molar ratio of P123/Zr are shown in Fig. 11. It is seen that the addition of P123 changed the pore size distribution, especially for the P123/Zr ratios of higher than 0.01 and shifted them to the higher values. For the samples prepared without addition of P123 and with a P123/Zr ratio of 0.01, an unimodal pore distribution was observed, but for the samples with higher ratio of P123/Zr a bimodal pore size distribution was observed.

The structural properties of the samples prepared with different P123/Zr molar ratio are reported in Table 3. The obtained results showed that the increasing in P123/Zr ratio increased the thermal stability of the zirconia, as the zirconia showed a higher specific surface area in higher P123/Zr molar ratio.

Figure 12 shows the TG and DTA curves of the samples prepared with and without addition of P123. For the sample prepared with addition of P123 the ratio of P123/Zr was chosen 0.03. As it can be seen, both the samples showed a

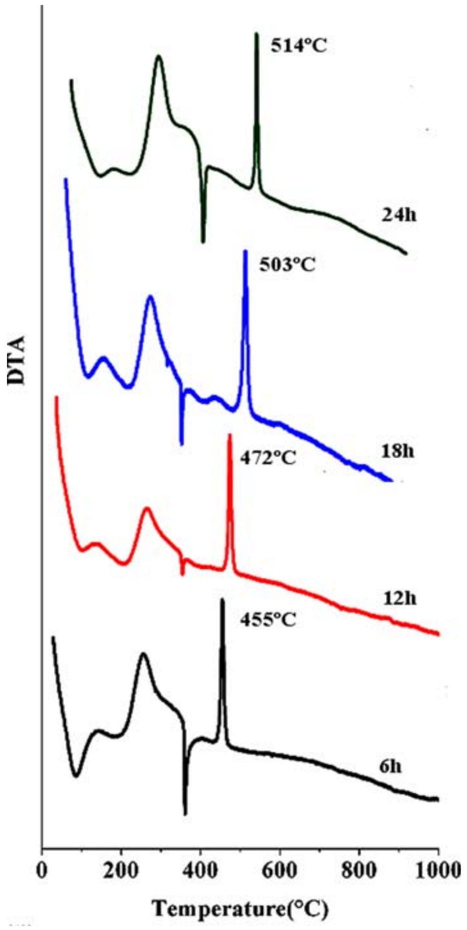

Fig. 9 DTA curves of the samples prepared under different refluxing times, refluxing temperature: 80 °C

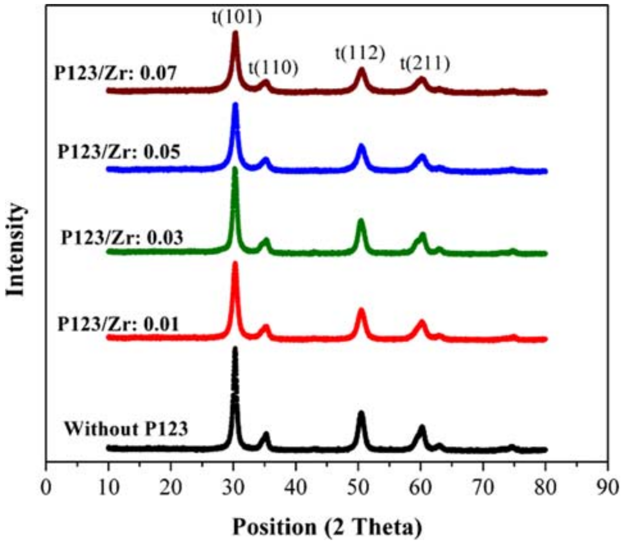

Fig. 10 XRD patterns of the samples prepared with various P123/Zr molar ratios

Table 3 Effect of P123/Zr molar ratio on the structural properties of the samples, refluxing temperature: 80 °C, refluxing time: 24 h

P123/Zr mole ratio	BET area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	Pore diameter (nm)	Crystalline size (nm)		
				t(101)	t(110)	t(112)
0	80.9	0.09	3.33	11.6	9.3	8.2
0.01	82.3	0.10	3.81	10	7.1	7.3
0.03	107.6	0.12	4.54	9.6	7.3	6.8
0.05	121.3	0.11	4.2	9.2	7	6.4
0.07	137.7	0.12	3.72	8.9	6.4	6.2

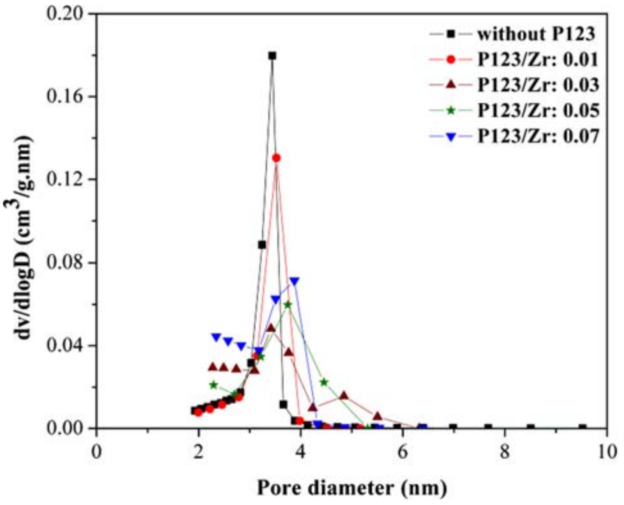

Fig. 11 Effect of P123/Zr molar ratio on the pore size distribution, refluxing time 24 h and refluxing temperature 80 °C

similar pattern of weight loss in TG curves, but the DTA results showed a significant difference between the crystallization temperatures of the samples. The obtained results showed that the addition of P123 increased the

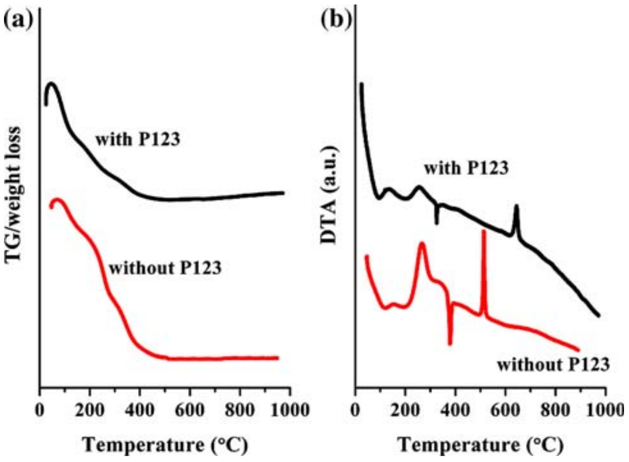

Fig. 12 (a) TG and (b) DTA curves of the samples prepared with and without addition of P123

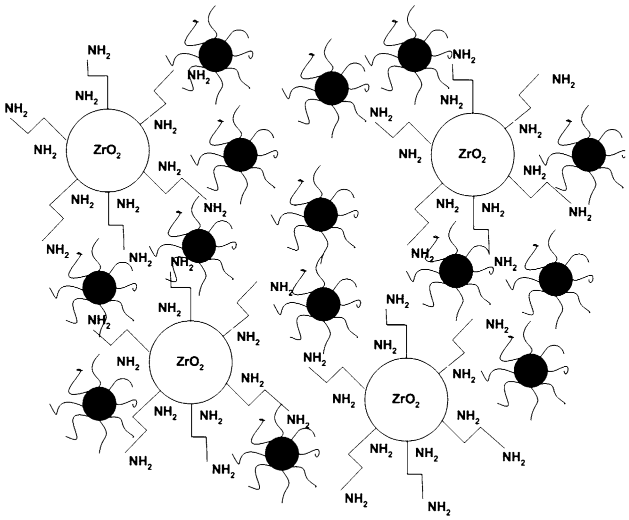

Fig. 13 Mechanism effect of ethylene diamine and P123 block copolymer for synthesis of nanozirconia

crystallization temperature of zirconia from 514 to 645 °C. The difference between the crystallization temperatures could be related to the difference between the crystallite sizes of the samples, as the XRD results, Table 3, showed smaller crystallite size for the sample prepared with addition of P123.

Mechanism of surfactant effect

Figure 13 shows a schematic of bifunctional effect of ethylene diamine and P123 block copolymer. The ethylene diamine can act as a protecting agent for zirconia particles by hindering the aggregation of particle during the synthesis process. In the other words, the ethylene diamine creates a certain distance between the layers, providing high flexibility of the layers and the interaction between the amine template and the zirconium atoms results in a structural reorganization of the zirconia layers leading to a distance between the layers and preventing the agglomeration of particles. Zirconia samples that were refluxed for higher refluxing times and temperatures demonstrated higher thermal stability. It could be due to this fact that refluxing time minimizes defect sites, which hinders grain growth during sintering. The ethylene diamine protecting agent acts as a steric barrier for the growth of the particles during the refluxing process. Hence, the crystallite maintains the original shape and size during refluxing, which results in higher surface area after calcination.

Addition of P123 block copolymer as a cosurfactant can decrease the interaction between the zirconia particles by formation of micelles between the ZrO_2 particles.

Conclusion

Mesoporous nanocrystalline zirconia with high surface area and pure tetragonal crystallite phase has been prepared by bifunctional ethylene diamine as both precipitating agent for $ZrO(NO_3)_2$ to $ZrO(OH)_2$ and colloidal protecting agent for the $ZrO(OH)_2$ nanoparticles. The obtained results showed that the increasing in refluxing time and temperature had a positive effect to improve the thermal stability by decreasing the crystallite size of the zirconia. The results also showed that the increasing in refluxing time increased the crystallization temperature of the zirconia, which could be explained by decreasing in crystallite size of the zirconia by increasing the refluxing time. Addition of P123 block copolymer as a cosurfactant had a positive effect to improve the thermal stability and decreased the crystallite size of the zirconia.

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