Effect of carboxylic acid modification on ZrO_2 nanoparticles synthesis in supercritical water

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Department of Environment Systems 47-206672 LI XUE
Assistant Professor Akizuki Makoto

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1 Research Background

Zirconium oxide (ZrO_2) has been used widely as catalysts and ceramics due to its specific chemical and physical properties, such as high thermal stability, ionic conductivity, and oxygen storage capacity [1]. ZrO_2 has several crystalline phases, including amorphous, monoclinic, tetragonal and cubic phase, leading to different functional performances. At ambient temperature and atmospheric pressure, ZrO_2 is usually stabilized in the monoclinic phase. Many applications of ZrO_2, such as thermal barrier coating, require tetragonal or cubic phases, which are normally produced from monoclinic phase through a reversible martensitic phase transformation at above 1200℃ [2]. However, it has been known for some time that the tetragonal phase exists at room temperature in microcrystals. Garvie estimated the phases stability of nanocrystalline ZrO_2 and proposed the hypothesis that below the size with about 10 nm, ZrO_2 nanoparticles exist as stable tetragonal phases at room temperature [3]. Wu *et al*. modified the ZrO_2 nanoparticles surface by hexamethyldisilazane and they found the modified ZrO_2 nanoparticles increased the room temperature tetragonal phase stability [4]. Bokhimi *et al*. found acetic acid participated in the stabilization of tetragonal phase based on the C-O bonding [5]. It is attributed that the surface modification decreases interfacial energies and reduces the surface nucleation sites to control the grain growth. Thus, for tetragonal ZrO_2 nanoparticles synthesis, getting small size and surface modification should be considered.

Supercritical hydrothermal synthesis is a developing technique for nanoparticles synthesis. In supercritical water (T≥374℃, P≥22.1MPa), the properties of water change rapidly. Near the critical point, dielectric constant and density decrease dramatically, which is because of the breakdown of extensive hydrogen bonding. These two properties decrease lead to polarity reduction, resulting in inorganic salt with lower solubility and more organics soluble in water [6]. Thus, faster nucleation and less time for particles growth achieve particles generation with small size in supercritical water. Additionally, with the solubility of organics increasing, organic modification and particles generation could happen at the same time. Surface modification makes an important role in nanomaterial synthesis because surface modified particles usually have smaller sizes, functional surface, and oriented structures [7]. For example, Taguchi *et al*. synthesized CeO_2 particles with cubic phase modified by lauric acid in supercritical water [8]. The carboxylic acids are usually used as modifiers but using dicarboxylic acid is less reported. Interestingly, Takami *et al*. found dicarboxylic acid combined two CeO_2 nanocrystals together [9].

This study explored the different effect of different carboxylic acids as modifiers on ZrO_2 nanoparticles synthesized in supercritical water. Carboxylic acids attached to the surface of metal oxides particles by coordination bonds between carboxylate anion (-COO$^-$) and metal cation. The influence of carboxylic acids with one or two carboxyl group (-COOH), short or long alkyl chain (-CH_2-) on the amount of modifiers attached to particles, size and phase of ZrO_2 nanoparticles has been investigated.

2 Experimental Methods

2.1 ZrO_2 Nanoparticle synthesis

Zirconyl nitrate dihydrate ($ZrO(NO_3)_2 \cdot 2H_2O$) as the precursor, hexanoic acid (HA), adipic acid (AA), sebacic acid (SA), decanoic acid (DA) as surface modifiers were used. The ethanol was also used as co-solvent due to low aqueous solubility of SA and DA. The chemical structures of modifiers

Table 1 Experiment conditions and morphology results

| | Sample Name | Feed Concentration / (mol/L) | | Size /(nm) | | Modification (mmol/g ZrO$_2$) |
		Zr^{2+}	Modifier	XRD	TEM	
1	UM-ZrO$_2$	0.002	-	5.5	7.5±2.3	-
2	002HA-ZrO$_2$	0.002	0.002 HA	5.7	6.9±2.2	19.6
3	006HA-ZrO$_2$	0.002	0.006 HA	6.1	7.5±2.2	17.9
4	002AA-ZrO$_2$	0.002	0.002 AA	5.9	6.8±3.1	25.8
5	006AA-ZrO$_2$	0.002	0.006 AA	5.2	7.4±2.9	27.6
6	E-ZrO$_2$	0.002	5%Ethanol	5.1	7.8±3.2	-
7	002SA-ZrO$_2$	0.002	0.002 SA+5%Ethanol	5.5	6.3±2.5	55.3
8	006SA-ZrO$_2$	0.002	0.006 SA+5%Ethanol	4.9	6.2±2.8	62.7
9	EAA-ZrO$_2$	0.002	0.002 AA+5%Ethanol	5.1	7.1±3.3	21.8
10	DA-ZrO$_2$	0.002	0.002 DA+5%Ethanol	7.8	-	22.4
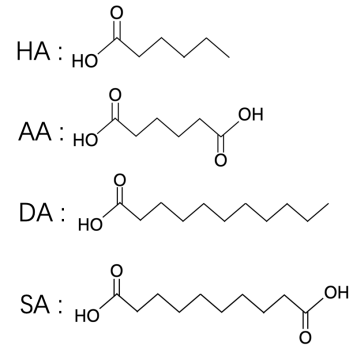
Fig. 1 The structure of modifiers

are shown as **Fig.1**. ZrO$_2$ nanoparticles were synthesized using a continues flow reactor, as depicted in **Fig.2**. The total feed flow rate is 100 g/min in ratio (Zr : modifier : water) of 1:1:8, and the experimental conditions are displayed in **Table 1**. The system pressure was maintained at 30 MPa and the temperature of reactor tube kept at 400℃ with residence time of 10 s. After reaction, the collected suspension was subjected to pressure filtration using the 0.025 μm nitrocellulose filter and dried in the vacuum oven for 24 h.

2.2 Characterization

The crystalline structure of nanoparticles was analyzed by XRD. The shape and sizes were observed through TEM. TG-DTA analysis was performed to test the amount of modifiers attached to particles and thermal changes in the heating process. FT-IR was used to investigate the chemical bonds between modifiers and particles surfaces.
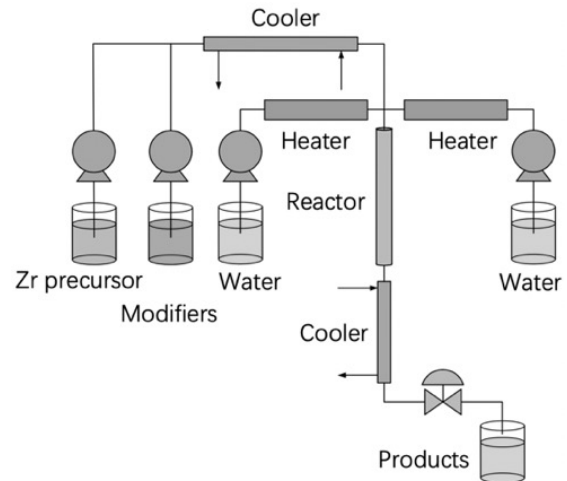
Fig.2 The apparatus of nanoparticles synthesis

3 Results and Discussion
3.1 Organic modification

To quantitatively estimate the amount of modifiers attached to surface, TG-DTA analysis have been performed. In the **Fig.3**, at the range of 250-400℃, DTA curves of all modified ZrO$_2$ show the exothermic peak but no obvious peak appears on UM-ZrO$_2$ and E-ZrO$_2$ curves. **Fig.4** shows that at same range of 250-400℃, all modified ZrO$_2$ have a distinct decrease on TG curves, exactly corresponding to peak position on DTA curves. The exothermic peaks in DTA curves and distinct mass loss in TG curves are attributed to modifiers combustion, which can be considered as the amount

Fig.3 The DTA curves

of modifiers, shown in **Table 1**. The surface modifiers of AA-ZrO$_2$ are more than of HA-ZrO$_2$, which
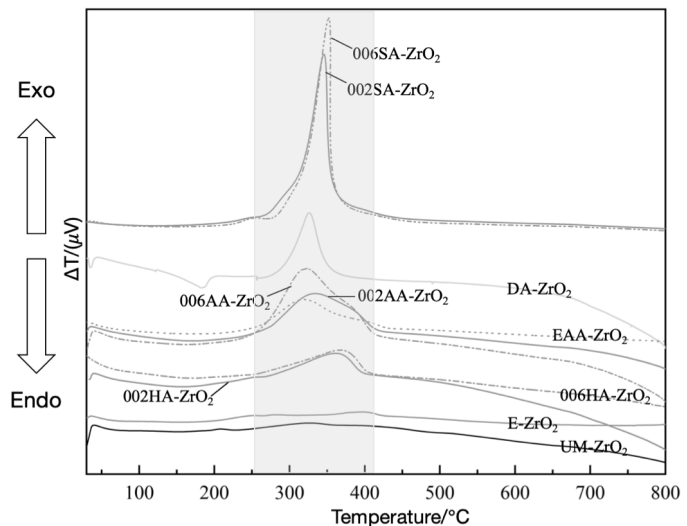
tells AA is probably easier to bind to ZrO_2 due to two -COOH. $AA-ZrO_2$ and $SA-ZrO_2$ with different modifiers feed concentration show that higher concentration leading to more modifiers attached to particles. In addition, the $UM-ZrO_2$ and $E-ZrO_2$ also has continuously mass loss for chemisorbed water. It's difficult to eliminate influence of water evaporation getting the accurate amount of modifiers. Nevertheless, $DA-ZrO_2$ shows not only exothermic peak but also the endothermic peak with approximately 50% mass loss from 100 to 200 ˚C, which is caused by the sublimation or evaporation of DA.

3.2 Interaction

The coordination bonds are assessed by FT-IR analysis as **Fig.5**. In the 1000-2000 cm^{-1} region, the pure AA, pure SA spectra and modified products have the peaks at 1408(v_s -COO$^-$), 1537(v_s -COO$^-$) and 1450 (δ_{sc} -CH$_2$-) cm^{-1}. In contrast, these peaks don't appear on $UM-ZrO_2$ and $E-ZrO_2$ spectra. The pure acid AA and SA shows a strong band at 1700 cm^{-1}, which is assigned to the stretching mode of the free carboxyl group (-COOH). It indicates modifiers are attached to the surface of the modified ZrO_2 nanoparticles by the coordination bonds of the -COO$^-$. In the 2500-4000 cm^{-1} region, the ZrO_2 products shows broad bands at 3400 cm^{-1}, which can be assigned to the O-H modes of chemisorbed water and terminated hydroxides ate the surface. $SA-ZrO_2$ spectrum also appears two absorbed peaks at 2920 (v_{as} -CH$_2$-), 2850 (v_s -CH$_2$-) cm^{-1}, which do not show on short chain acid AA and HA modified products, probably attributed to the long alkane chain of SA. In addition, compared with pure carboxylic acid with two -COOH, free -COOH are not observed in products modified by AA but by SA. It suggests probably more AA combined to ZrO_2 nanoparticles with both two carboxyl groups than SA.

3.3 Phase and size

All products after drying appear like sheeting shape with little yellow or brown except $DA-ZrO_2$. The dried $DA-ZrO_2$ is white paste, which is probably attributed to massive DA residual. The XRD patterns of prepared ZrO_2 nanoparticles are plotted in **Fig.6**. The broad diffraction peaks in the XRD patterns indicate particles with small crystallite sizes. The modified and unmodified ZrO_2 samples mainly show monoclinic phase, for peaks can be observed at 2θ values of 28.2˚ and 31.5˚, corresponding to the monoclinic phase plane M(-111) and M(111). $AA-ZrO_2$, $EAA-ZrO_2$ and $E-ZrO_2$ show the shoulder peak at 2θ values of 30.1˚.
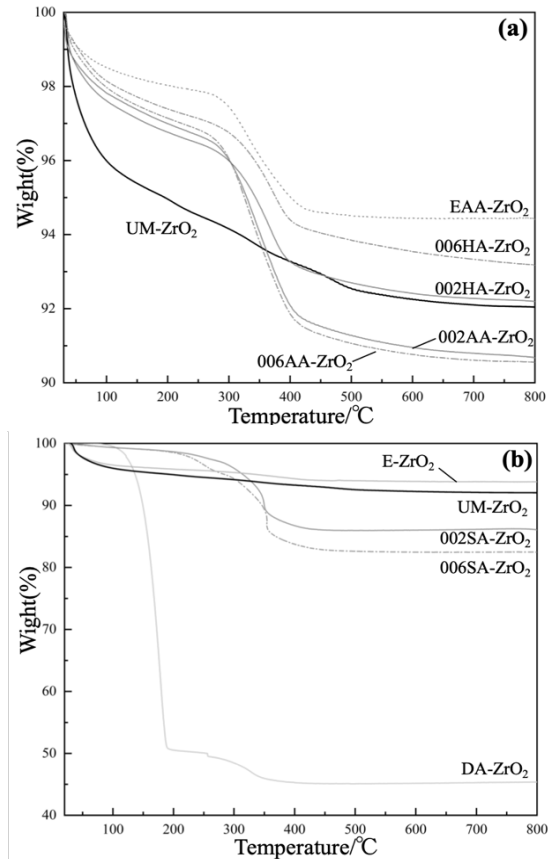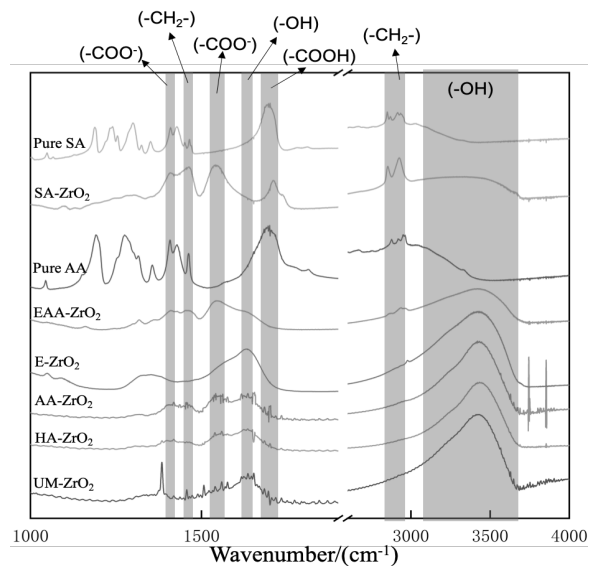

Fig.4 The TG curves

Fig.5 The FTIR spectra

DA-ZrO_2 and SA-ZrO_2 show peak with strong intensity at the same place, which is corresponding to the tetragonal phase plane T(101). The carboxylic acid modification probably has an effect on crystal structures, oriented to generating tetragonal phases. The addition of ethanol has the effect on tetragonal phase formation, which is also reported in other researches [10]. Compared SA-ZrO_2 to EAA-ZrO_2, both with 5% ethanol, long chain carboxylic acid revealed stronger tetragonal peak in XRD patterns. The possible reason of effect on crystal phase is that when modifiers bind to the particles plane T(101), the growth rate of T(101) decreases, leading to tetragonal ZrO_2.

The TEM images of four samples are shown in **Fig.7**, unmodified, monoacid-modified, with ethanol and diacid-modified samples with ethanol. Regardless of modifier species or existence of ethanol, ZrO_2 nanoparticles has almost the same sizes and appearance. All morphologies of products appear like distorted spheres and some particles appear with sharp edges, which can be recognized as hexagon or octagon. TEM results also show the ZrO_2 nanoparticles cluster into dense agglomerates with or without modification. TEM images, the size estimates obtained from XRD and TEM are no significant differences as **Table 1**. Modifiers seem to have little effect on size at such small scales, or possibly the modification is not sufficient.

Fig.6 The XRD pattern

Fig. 7 The TEM images

4 Summary and Conclusion

This study synthesized the ZrO_2 nanoparticles modified by carboxylic acids in supercritical flow reactors. Using short chain (6 C) and long chain (10 C) acid with one or two carboxyl groups as modifiers, ZrO_2 nanoparticles has no remarkable change on size or appearance but changes on crystalline phase can be observed. SA and DA have obvious effect on the stabilization of tetragonal phase. HA and AA, have less selective on tetragonal ZrO_2 but selective on monoclinic as the same as the unmodified ZrO_2. The FTIR also indicate the AA combined particles both two -COOH but SA modified ZrO_2 exists plenty of free -COOH.

Overall, the carboxylic acid has no obvious effect on the ZrO_2 nanoparticles morphology but the modified ZrO_2 phase have tetragonal-oriented. And this is considerable to use longer chain acid as modifiers for getting more tetragonal phases. For the modification, di-acids might combine ZrO_2 particles more easily due to two -COOH leading to more chances to contact the particles. Versatile types of carboxylic acids offer the possibility to modify the nanoparticles in supercritical water.

References

[1] M Taguchi, *Cryst. Eng. Comm.,* 14:2132–2138(2012). [2] E. C. Subbarao, H. Maiti, K. Srlvastava, *Phys. Status Solidi A*, 21(1975). [3] R. Garvie, *J. Phys. Chem.*, 82:218-224(1978). [4] N. Wu, T. Wu, I. Rusakova, *J. Mater. Res.*, 16(2001). [5] X. Bokhimi, A. Morales, O. Novaro, *Nanostruct. Mater.*, 12:593-596(1999) [6] J. Darr, J. Zhang, N. Makwana, *Chem. Reviews*, 117:11125-11238(2017). [7] D. Rangappa, S. Ohara, T. Naka, *J. Mater. Chem.*, 17:4426-4429(2007). [8] M. Taguchi, N. Yamamoto, D. Hojo, *RSC Adv.*, 4:49605-49613(2014). [9] S. Takami, S. Ohara, T. Adschiri, *Dalton Trans.*, 40:5442-5446(2008). [10] A. Auxéméry, G. Philippot, *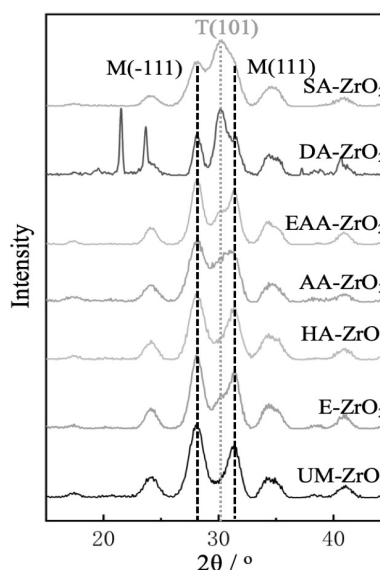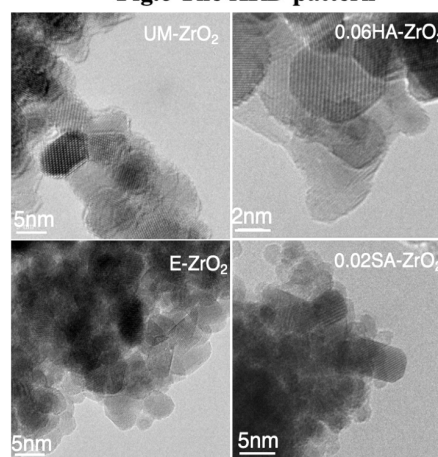J. Mater. Chem.*, 32:8169-8181(2020).