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# Synthesis and characterization of Al<sub>2</sub>O<sub>3</sub>-Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> powders prepared by chemical coprecipitation method

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# ABSTRACT

Al<sub>2</sub>O<sub>3</sub>-Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> catalytic powders were synthesized by the coprecipitation (ACZ-C) and mechanical mixing (ACZ-M) methods, respectively. As-synthesized powders were characterized by XRD, Raman spectroscopy, surface area and thermogravimetric analyses. It was found that the mixing extent of Al3+ ions affected the phase development, texture and oxygen storage capacity (OSC) of the  $Ce_{0.5}Zr_{0.5}O_2$  powder. Single phase of ACZ-C could be maintained without phase separation and inhibit  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> formation up to 1200 °C. The specific surface area value of ACZ-C (81.5 m<sup>2</sup>/g) was larger than that of ACZ-M (62.1 m<sup>2</sup>/g) and  $Ce_{0.5}Zr_{0.5}O_2$  (17.1 m<sup>2</sup>/g) powders, which were calcined at 1000 °C. In comparison with ACZ-C and Al<sub>2</sub>O<sub>3</sub>, which were calcined at high temperature (900–1200 °C), it was found that the degradation rate of specific surface area of ACZ-C was lower than that of Al<sub>2</sub>O<sub>3</sub>. ACZ-C sample showed a higher thermal stability to resist phase separation and crystallite growth, which enhanced the oxygen storage capacity property for Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> powders.

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# 1. Introduction

Promoting the catalyst conversion performance of the vehicle exhaust is important for the increasingly restricted emission regulations. The next generation of emission catalysts must have following two characteristics: (i) high thermal stability to resist the high temperature sintering and the deactivation resulting from the closely coupled converter (CCC), (ii) high surface area to increase the reaction efficiency, and achieve higher noble metal dispersion, thereby decreasing noble metal usage [1].

CeO<sub>2</sub> has been widely applied in many fields, including catalysis, fuel cell and glass polishing technologies. In current three-way catalyst (TWC) for automotive pollution control, the unique reducing and oxidizing properties of CeO<sub>2</sub> allow the catalyst to enlarge the operating air/fuel (A/F) ratio window [2]. In a reducing atmosphere, CeO<sub>2</sub> releases oxygen to form CeO<sub>2-x</sub> (x < 2). However, CeO<sub>2-x</sub> can easily absorb oxygen and form CeO<sub>2</sub> in an oxidizing atmosphere. This is the so-called oxygen storage capacity (OSC) characteristics

The redox property of CeO<sub>2</sub> is greatly enhanced by incorporation of zirconium ions (Zr<sup>4+</sup>) into the lattice to form a solid solution [3-6]. Nagai et al. [7] have suggested that enhancing the homogeneity of Ce and Zr atoms in the CeO<sub>2</sub>-ZrO<sub>2</sub> solid solution can improve OSC performance. Besides, Fornasiero et al. [2] have reported that an optimum composition, like Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> (molar ratio of Ce:Zr = 1:1) can exist as a cubic phase, which can have best redox property. Therefore, the homogeneity of the composition and crystalline phase play crucial roles in the CeO<sub>2</sub>-ZrO<sub>2</sub> solid solution for TWC applications. Some researches [1,3,8,9] have proposed that addition of Al<sub>2</sub>O<sub>3</sub> can promote the thermal stability and specific surface area of CeO<sub>2</sub>-ZrO<sub>2</sub> solid solution. Various preparation methods (coprecipitation, impregnation and sol-gel methods) [9,10] have been employed in order to synthesize a homogeneous CeO<sub>2</sub>-ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. These methods can both combine the advantages of high specific surface area of Al<sub>2</sub>O<sub>3</sub> and high OSC property of the CeO<sub>2</sub>–ZrO<sub>2</sub> solid solution.

Recently, Morikawa et al. [11] investigated the effect of introducing alumina into CeO<sub>2</sub>-ZrO<sub>2</sub> solid solution as a diffusion barrier on the physical properties and OSC characteristics and observed that the improvement of OSC could be achieved by suppression of grain growth of CeO<sub>2</sub>–ZrO<sub>2</sub> and Pt particles via introducing Al<sub>2</sub>O<sub>3</sub> as a diffusion barrier at nanometer scale. However, the effects of alumina doping and mixing extent of Al<sup>3+</sup> on the development of phase separation and texture characteristics of  $Ce_{0.5}Zr_{0.5}O_2$  are not clear. Therefore, in this study, the effect of mixing extent of Al<sup>3+</sup> ions on the crystallite size, phase development and texture characteristics of Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> after heat treatment at 500-1200 °C were investigated. In addition, the effects of these microscopic characteristics on the macroscopic OSC property were discussed as well.

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#### 2. Experimental procedures

# 2.1. Sample preparation

The ACZ-C sample ( $Al_2O_3$ -Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>, molar ratio of Al:Ce:Zr = 4:1:1) was synthesized by the coprecipitation method [8,9]. In a typical synthetic condition, the stoichiometric amount of ammonium cerium(IV) nitrate ((NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub>, J.T. Baker, >99%), zirconium(IV) dinitrate oxide (ZrO(NO<sub>3</sub>)<sub>2</sub>, Sigma-Aldrich, >99%) and aluminium nitrate(Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Showa, >98%) were dissolved in distilled water. These solutions were mixed and slowly dripped into an aqueous NH<sub>4</sub>OH solution. The pH value of the co-precipitating solution was maintained at 9 by adding 10% NH<sub>4</sub>OH solution. The obtained precipitate was filtered and thoroughly washed using distilled water and isopropanol to remove the anion impurities, and finally dried at 80 °C for 48 h. The obtained cakes were ground into powder, then the powder was calcined at different temperatures (500-1200 °C) for 2 h (heating rate 5 °C/min) in air atmosphere. The same synthesis route was employed for the preparation of the CZ (molar ratio of Ce:Zr = 1:1) and Al<sub>2</sub>O<sub>3</sub> reference samples. However, the ACZ-M sample (molar ratio of Al:Ce:Zr=4:1:1) was synthesized using a mechanical mixing method. As prepared precursor powders of CZ and Al<sub>2</sub>O<sub>3</sub> (not calcined) were mechanical mixed in an agate mortar for 20 min.

#### 2.2. Characterization

Powder X-ray diffraction (XRD) data was collected using Siemens D5000 (CuK $\alpha_1$  radiation, 40 KV, 40 mA). Crystallite size was estimated from XRD data using the Scherrer equation [3]. For Raman spectroscopic characterization, a laser beam of 532 nm wavelength (laser power: 100 mW), served as the excitation light source, which was focused using a ×100 microscopic objective. The BET specific surface area and pore volume measurements were performed using a standard nitrogen adsorption–desorption technique (Micromeritics ASAP2020). Thermogravitmetry analysis (Netzsch STA 409C) was used to characterize the OSC [12] by monitoring the changes in weight under cyclic heat treatment in flowing air. The heat cycle consisted of first heating treatment to 900 °C, cooling to 150 °C, and a second heating treatment to 900 °C. The heating and cooling rates were 5 °C/min. The weight loss of samples in the second heating TG data was used as a measure of oxygen release properties of the powders between 300 and 800 °C.

#### 3. Results and discussion

#### 3.1. XRD characterization

Fig. 1 shows XRD patterns of the CZ samples, which have been calcined in the temperature range of 500-1200 °C. A single phase of Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> solid solution has been observed when the calcination temperature is below 1000 °C. As the calcining temperature is raised above 1100 °C, the phase separates into Ce-rich and Zrrich phases [5]. Fig. 2 shows the XRD patterns of ACZ-M samples, which have been calcined at different temperatures and indicate



Fig. 1. XRD patterns of CZ samples after calcination at different temperatures.



Fig. 2. XRD patterns of ACZ-M samples after calcination at different temperatures.

that the ACZ-M follow the same trend like CZ. Thus, the phase separation of  $Ce_{0.5}Zr_{0.5}O_2$  has occurred at 1100 °C. The phase formation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (see Fig. 2) has been observed at 1200 °C.

XRD patterns of the ACZ-C samples which have been calcined in the temperature range of 500–1200 °C are shown in Fig. 3. Interestingly, a single phase of Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> accompanies with a  $\theta$ -Al<sub>2</sub>O<sub>3</sub> phase has been observed in ACZ-C. For Al<sub>2</sub>O<sub>3</sub> sample, the phase formation temperature of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is at 1100 °C (Fig. 4). For ACZ-M sample, the formation temperature of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> has been shifted to 1200 °C (Fig. 2). It provides the evidence that the formation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and the phase separation of Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> are inhibited in ACZ-C sample up to 1200 °C.

The crystallite sizes of  $Ce_{0.5}Zr_{0.5}O_2$  as a function of calcination temperature for ACZ-C, ACZ-M and CZ samples are shown in Table 1 and Fig. 5. The crystallite growth curves for the CZ and ACZ-M samples are nearly overlapped in the temperature range of 500–1100 °C. Besides, above 1000 °C the crystallite sizes of  $Ce_{0.5}Zr_{0.5}O_2$  are found to increase rapidly with increasing temperatures. The phase separation of  $Ce_{0.5}Zr_{0.5}O_2$  has also been observed in the temperature range of 1000–1100 °C. Kenevey et al. [5] have observed that in the



Fig. 3. XRD patterns of ACZ-C samples after calcination at different temperatures.



Fig. 4. XRD patterns of Al<sub>2</sub>O<sub>3</sub> samples after calcination at different temperatures.

#### Table 1

Crystallite sizes of Ce  $_{0.5} Zr_{0.5} O_2$  for CZ, ACZ-C and ACZ-M samples after calcination at different temperatures

Sample (°C)	$CZ(nm)^*$	ACZ-C (nm)*	ACZ-M (nm)
500	4.8	2.6	5.2
700	7.1	4.3	7.1
900	12.8	8.0	12.4
1000	11.1	11.2	11.7
1100	27.5	13.4	22.3
1200	92.3	23.1	68.4

Measured from Scherrer equation of XRD.

case of  $Ce_{0.5}Zr_{0.5}O_2$ , there exists a critical size around 150 Å, beyond which phase separation occurs due to the surface energy effect.

It should be noted that for CZ and ACZ-M samples, the crystallite sizes have decreased from ~120 to ~110 Å as the calcination temperature is increased from 900 to 1000 °C. This may be due to the phase separation in CZ and ACZ-M samples during calcination in the temperature range of 900–1000 °C, which can lead to the broadening of XRD diffraction peak [5]. For ACZ-C sample, minor crystallite growth with increasing calcination temperature (see Fig. 5) has been observed. This reveals that the mechanical mixing has not effectively inhibited the crystallite growth of Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>, but the



Fig. 5. Crystallite sizes of Ce $_{0.5}$ Zr $_{0.5}$ O $_2$  for ACZ-C, ACZ-M and CZ samples after calcination at different temperatures.



Fig. 6. Raman spectra of (a) CZ, (b) ACZ-M and (c) ACZ-C samples after calcination at 900  $^\circ\text{C}.$ 

coprecipitation route has suppressed the crystallite growth successfully.

# 3.2. Raman spectroscopy

Because XRD is not sensitive to light elements (i.e. oxygen) in the presence of heavy elements (i.e. cerium), it is difficult to separate the t" phase from the cubic phase (c phase) of the  $Ce_{0.5}Zr_{0.5}O_2$ by using XRD alone. However, the Raman spectroscopy is sensitive to the tetragonal distortion of the oxygen positions and can be employed to distinguish between c and t" phases of  $Ce_{0.5}Zr_{0.5}O_2$ [6,13,14].

Fig. 6 shows the Raman spectra of CZ, ACZ-M and ACZ-C samples, which have been calcined at 900 °C. ACZ-C (Fig. 6(c)) shows only one prominent peak at 471 cm<sup>-1</sup>, which is attributed to the  $F_{2g}$  vibration mode of cubic fluorite structure [14]. However, the CZ (Fig. 5(a)) and ACZ-M (Fig. 5(b)) samples show two additional peaks at ~300 and ~610 cm<sup>-1</sup> which can be assigned to the Raman modes of the t" phase [6]. Thus, Raman spectra (Fig. 6(a) and (b)) along with XRD patterns (Figs. 1 and 2) confirm the formation of t" phase.

Fig. 7 shows the Raman spectra of the CZ, ACZ-M and ACZ-C samples which have been calcined at 1100 °C. The Raman peaks at ~250, 300, 475 and 610 cm<sup>-1</sup> are typical vibration modes of tetragonal structure for CZ and ACZ-M sample(Fig. 7(a) and (b)).



Fig. 7. Raman spectra of (a) CZ, (b) ACZ-M and (c) ACZ-C samples after calcination at 1100  $^\circ\text{C}.$ 

Furthermore, ACZ-C is considered to possess the t<sup>''</sup> phase which is supported together with XRD results (Fig. 3). When calcination temperature is increased from 900 to 1100°C, the Raman peak at  $\sim$ 471 cm<sup>-1</sup> becomes sharper, more symmetrical and is slightly shifted to a higher wavenumber. This can be due to better crystallinity of Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> at higher calcination temperatures [14], which is in consistency with the XRD observation. Comparison of the Raman spectra of ACZ-C, ACZ-M and CZ samples reveals that the Raman peak of ACZ-C is more asymmetrically broadening than that of the others. This can be due to the size-effect in small crystallite [15]. Based on the XRD and Raman results, it is suggested that the phase separation of Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> has been inhibited and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> formation is prevented in ACZ-C sample up to 1200 °C. Only the ACZ-C has formed the cubic fluorite structure of  $Ce_{0.5}Zr_{0.5}O_2$  at 900 °C. However, it has been observed that the phase separation of  $Ce_{0.5}Zr_{0.5}O_2$  at 1100 °C and the appearance of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at 1200 °C take place in ACZ-M sample. This suggests that there are no significant improvement for ACZ-M sample in comparison with the reference samples of CZ and Al<sub>2</sub>O<sub>3</sub>.

The growth of crystallite in nano-crystalline materials can be regarded as the coalescence of small neighboring crystallites due to atomic diffusion or discrete attachment of crystallographically oriented particles [16]. The nano-crystallites, with their low mass and very large surface area, may coalesce to decrease their surface energy. In oriented attachment based coarsening, two small nanocrystallites combine to form a larger crystallite without the need for atomic diffusion. Apparently, the growth of crystallite based on the oriented attachment mechanism is dependent upon the probability of contact between nano-crystallites in appropriate orientations. We assume that the mixing extent of ACZ-C sample via coprecipitation method is near the atomic level mixing. Thus, Al<sup>3+</sup> ions in Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> powder may effectively protect the Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> particles from aggregation, and suppress the crystallite growth via the oriented attachment mechanism. In contrast, the mixing extent in



Fig. 8. Specific surface area of Al<sub>2</sub>O<sub>3</sub>, ACZ-C, ACZ-M and CZ samples after calcination at different temperatures.

ACZ-M is at micron scale mixing, which cannot suppress the crystallite growth and phase separation.

#### 3.3. Textural property

# 3.3.1. BET specific surface area

The BET specific surface area values of  $Al_2O_3$ , ACZ-C, ACZ-M and CZ samples, which have been calcined at different temperatures, are shown in Fig. 8 and Table 2. The BET specific surface area of ACZ-C and ACZ-M samples are found to be higher than that of CZ. This can be attributed to the effect of  $Al_2O_3$  addition. Furthermore, the specific surface area of ACZ-C is higher than that of ACZ-M. The highest BET specific surface area has been obtained for  $Al_2O_3$  sample due to the small crystallite size of  $\gamma$ -Al\_2O<sub>3</sub> (Fig. 4). However, the

 Table 2

 Textural properties of CZ, ACZ-C, ACZ-M and Al<sub>2</sub>O<sub>3</sub> samples after calcination at different temperatures

Sample	BET (m <sup>2</sup> /g)				Pore volume (cm <sup>3</sup> /g)		Centered p	Centered pore size (nm)			
	500 °C	700°C	900°C	1000 °C	1100°C	1200°C	900°C	1100 ° C	900 °C	1100 °C	
CZ	142.1	91.1	41.5	17.1	3.9	-	0.30	0.02	29	_*	
ACZ-C	252.3	181.6	120.2	81.5	57.0	24.9	1.16	0.68	43	90	
ACZ-M	207.6	157.8	104.6	62.1	44.6	7.6	0.78	0.36	29	29	
$Al_2O_3$	334.0	264.2	188.5	128.0	97.1	7.4	1.37	0.68	30	30	

<sup>\*</sup> The center pore size of CZ at 1100 °C was unapparent.



Fig. 9. (a) Cumulative pore volume for Al<sub>2</sub>O<sub>3</sub>, ACZ-C, ACZ-M and CZ samples after calcination at 900 °C and (b) pore size distribution for Al<sub>2</sub>O<sub>3</sub>, ACZ-C, ACZ-M and CZ samples after calcination at 900 °C.



Fig. 10. (a) Cumulative pore volume for Al<sub>2</sub>O<sub>3</sub>, ACZ-C, ACZ-M and CZ samples after calcination at 1100 °C and (b) pore size distribution for Al<sub>2</sub>O<sub>3</sub>, ACZ-C, ACZ-M and CZ samples after calcination at 1100 °C.

specific surface area of the Al<sub>2</sub>O<sub>3</sub> has dropped drastically at 1200 °C (see Fig. 8), which is due to the extensive formation of coagulated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. This is a major issue of Al<sub>2</sub>O<sub>3</sub> powders for thermal stability at high temperature.

## 3.3.2. Porosity measurement

The pore volume measurement results for the Al<sub>2</sub>O<sub>3</sub>, ACZ-C, ACZ-M and CZ samples are summarized in Table 2. Fig. 9(a) and (b) shows the cumulative pore volume and the pore size distribution of the samples, which have been calcined at 900 °C, respectively. The total pore volume sequence is: Al<sub>2</sub>O<sub>3</sub> > ACZ-C > ACZ-M > CZ. The Al<sub>2</sub>O<sub>3</sub> sample shows the largest pore volume due to the small crystallite size of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The peak position of the pore size distribution curve centers at 30 nm for Al<sub>2</sub>O<sub>3</sub> sample (see Fig. 9(b)). ACZ-M has the same peak position of pore size distribution curve. This indicates that the texture behavior of ACZ-M is mainly dominated by Al<sub>2</sub>O<sub>3</sub>. This can be attributed to the poor mixing homogeneity (micron scale) of ACZ-M. The agglomeration of Al<sub>2</sub>O<sub>3</sub> and Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> effectively. However, the peak position of pore size distribution curve centers at 45 nm for ACZ-C, which is slightly larger than that for Al<sub>2</sub>O<sub>3</sub>.

The pore structure of the above samples, which are calcined at 1100 °C (Fig. 10(a) and (b)), are destroyed by extensive sintering, especially for the CZ sample. The total pore volume sequence is: ACZ-C, Al<sub>2</sub>O<sub>3</sub> > ACZ-M > CZ. Besides, the degradation rate of pore volume of ACZ-C is lower than that of Al<sub>2</sub>O<sub>3</sub> in the temperature range of 900-1100 °C. This demonstrates that the thermal resistance of ACZ-C sample is better than that of Al<sub>2</sub>O<sub>3</sub> sample. The porosity of CZ sample is almost disappeared after calcination at 1100 °C. The peak position of pore size distribution curve for Al<sub>2</sub>O<sub>3</sub> sample centers at  $\sim$ 30 nm, which can be due to the presence of remaining  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The ACZ-M sample follows similar behavior with Al<sub>2</sub>O<sub>3</sub> sample. For ACZ-C sample, the peak position in pore size distribution curve moves to 90 nm (at 1100 °C) from 45 nm (at 900 °C). We attribute this to the elimination of small pores during high temperature sintering. From the above results, it can be concluded that the addition of Al<sub>2</sub>O<sub>3</sub> in Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> powder would stabilize the texture structure. The specific surface area and pore volume of the ACZ-C are better than that of the ACZ-M.

# 3.4. OSC property

The OSC measurement data are shown in Table 3. The OSC values of ACZ-C and ACZ-M samples are twice higher than that of CZ. Additionally, the OSC value of ACZ-C is somewhat higher than that of

Table 3	
OSC ( $\mu$ mol/g) measurement results of CZ, ACZ-C and ACZ-M	samples

Sample (°C)	CZ (nm)	ACZ-C (nm)	ACZ-M (nm)
900 1100	211.2 130.9	441.2 347.5	400.2 330.4

The OSC value was calculated by conversing the sample to Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> per gram.

ACZ-M. This reveals that the addition of Al<sub>2</sub>O<sub>3</sub> into Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> solid solution would promote the OSC [8,9]. The ACZ-C sample which has been calcined at 900 °C has the highest OSC value due to formation a single phase of Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> exhibiting cubic fluorite structure, which has a larger oxygen mobility channel than the tetragonal phase [2]. The specific surface area of the ACZ-C sample is larger than those of the ACZ-M and CZ samples. The degradation rate of the specific surface area of ACZ-C is lower than that of Al<sub>2</sub>O<sub>3</sub> at high temperature (900–1200 °C). Therefore, the ACZ-C sample has a higher OSC stability than ACZ-M and CZ samples. From the above results, it is suggested that the enhancement of the mixing level of Al<sub>2</sub>O<sub>3</sub>-Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> and maintaining the cubic fluorite structure of Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> solid solution without phase separation can promote the OSC property effectively.

# 4. Conclusions

The mixing extent of constituents in  $Al_2O_3$ - $Ce_{0.5}Zr_{0.5}O_2$  powders plays a crucial role in the thermal stability, phase composition, texture and OSC property.

The ACZ-C sample can form single cubic fluorite phase at 900 °C without phase separation and has the highest OSC property.

The atomic level mixing in ACZ-C by chemical coprecipitation method can inhibit crystallite growth and prevent phase separation during calcination, thereby obtaining better OSC property.

In comparison with the ACZ-C and ACZ-M, the micron scale mixing in the latter during mechanical mixing process cannot inhibit the crystallite growth and phase separation effectively. Therefore, the stability of specific surface area, total pore volume and OSC property of ACZ-M are found to be inferior to ACZ-C.

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