Study on nano-Al_2O_3 modified by supercritical fluid

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Nano-Al_2O_3 was modified by supercritical ethanol and supercritical water, respectively. The mechanism between supercritical fluid and nano-Al_2O_3 was analyzed, and the microstructure of nano-Al_2O_3 was investigated. The mechanism between supercritical fluid and nano-Al_2O_3 was that the hydrogen bond between the molecules of fluid became attenuating, when the fluid was in the supercritical state. The surface of nano-Al_2O_3 was coated with fluid molecules through the bonding between the hydroxyl of nano-Al_2O_3 and fluid molecules. The effect of surface modification of nano-Al_2O_3 was the best when the nano-Al_2O_3 was modified by supercritical ethanol and the processing time was 5min.

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Keywords: Supercritical water, Supercritical ethanol, Hydrogen bond, Nano-Al_2O_3

1. Introduction

When temperature and pressure of the fluid exceed its critical temperature T_c and critical pressure P_c, the fluid is defined as supercutical fluid (SCF) [1]. Supercritical fluid has characteristics of gas and liquid state such as the density is close to liquid, dissolving capacity is similar to the liquid and the viscosity and diffusion coefficient are similar to gas, meanwhile. SCF is widely used in the field of biochemical reaction, environmental protection, materials science and others. The critical condition of supercritical ethanol (SCE) is kind (T_c= 513. 9 K, P_c= 6. 14 MPa, ρ_c= 276 kg / m^3), and SCE has the peculiarity of weak hydrogen bonding and high dielectric constant. The critical condition of supercritical water (SCW) is higher (T_c= 647.1 K, P_c= 22.06MPa, ρ_c= 322 kg / m^3), but the cost is lower, SCE and SCW are two kinds of supercutical fluid. Nano-particles may have a significant impact on the electrical properties, heat resistance and mechanical properties of the composites, but the nano-Al_2O_3 particles prone to reunite in the matrix resin and scattered unevenly, since the surface energy of nano-Al_2O_3 is huge, the instability is strong and the surface of nano-Al_2O_3 is oleophobic, the excellent performances of nano-Al_2O_3 cannot develop entirely [2-5]. The surface modification can enhance the dispersion of nano-powders and becomes a hot point of nano-composite manufacturing technology. Fluid molecules can adhere to the surface of nano-composite by the special effects of SCF, replace the effect between nano-Al_2O_3 particles, and reduce the reunion phenomenon effectively. There is no report about using SCF to modify nano-particles. The nano-Al_2O_3 was modified by supercritical ethanol and supercritical water in this paper, respectively, the mechanism and microstructure of nano-Al_2O_3 were studied by FT-IR, SEM and TEM methods.

2. Experiment

2.1. Materials and instrument

Nano-Al_2O_3 (30nm) was purchased from Hangzhou Wanjing New materials co., LTD, industrial product. Anhydrous ethanol and Liquid paraffin were from Harbin chemical reagent factory, chemical pure.

Electronic analytical balance (AE200, Shanghai) was purchased from Mettler Toledo instrument co., LTD. The supercritical device was made by oneself. The structure of supercritical device was shown in Fig. 1.

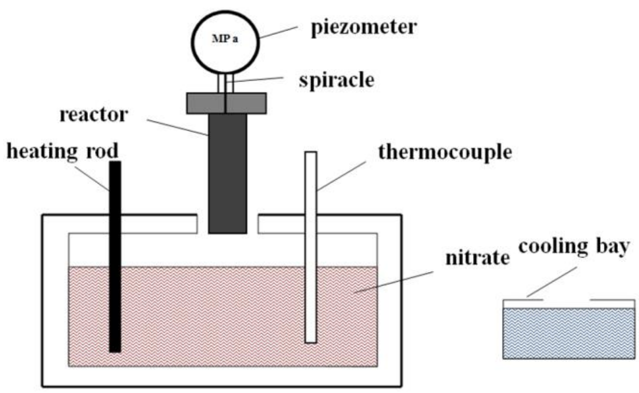


Fig. 1. The structure diagram of supercritical device.

2.2. Measurements

The FT-IR spectra, which was used to study the mechanism between supercritical fluid and nano-Al_2O_3, was performed with a EQUINOX-55 Fourier transform spectrometer (GER), in the 400-4000 cm^{-1} range, 5 scans were averaged for each spectrum. And it could be seen that there existed the characteristic absorption bands of material.

The state of aggregation and morphology of nano-Al_2O_3 was tested by JEM-2100 Transmission electron microscopy (TEM, Japan), the testing temperature was 18 □ and testing voltage was 120 kV.

Microstructure of nano-Al_2O_3 was studied by FEI Sirion scanning electron microscope (SEM, USA). The sample was placed on the sample stage and tested the sample after spraying.

Sedimentation experiment was carried out in liquid paraffin, in order to evaluate the dispersion of the nano-particles in nonpolar solvent. The volume of liquid was 20ml and the weight of Al_2O_3 was 1g, vibrated adequately under ultrasonic conditions and sedimentation time was 24h.

2.3 Surface treatment of nano-Al_2O_3

Nano-Al_2O_3 was dried at 80℃ for 10h in an oven before being used, 5.00g Al_2O_3 was added into a supercritical reactor at first, then added 50ml ethanol and stirred, the reactor should be sealed. While the temperature of heated pool reached to 513.9K, put the reactor into heated pool. Kept five minutes when the pressure of reactor reached to 6.14MPa. Then took out the reactor and put into a bucket which was equipped with cold water. Nano-Al_2O_3 was dried for 8h at 80℃ in a vacuum oven.

3. Results and discussions

3.1 FTIR spectral analysis

FT-IR spectra of Al_2O_3 are presented in Fig. 2. The curves of a, b, c are designated as *pure*-Al_2O_3, Al_2O_3 modified by supercritical ethanol (*SCE*-Al_2O_3), and Al_2O_3 modified by supercritical water (*SCW*-Al_2O_3), respectively.

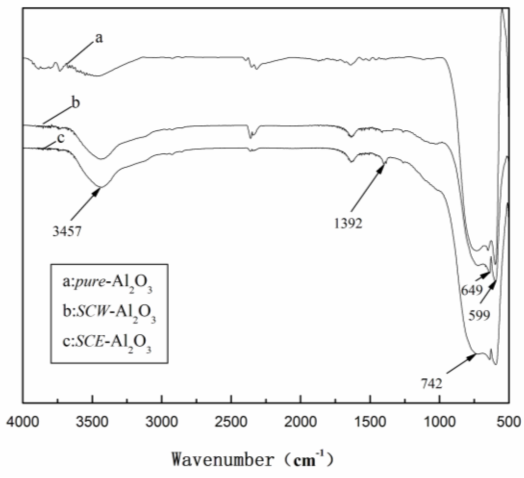


Fig. 2. FT-IR spectra of nano- Al_2O_3.

Fig. 2 showed that curve a, b and c had characteristic peaks at 599, 649 and 742 cm^{-1}, and these peaks were due to the stretching vibration of Al-O[6]. The peak at 3,457cm^{-1} of curve a was due to –OH stretching vibration, which was lower than curve b and c, the reason was that the hydrogen bonding between fluid molecules became weak [7], when fluid achieved the supercritical condition. Then the fluid molecule adhered to the surface of Al_2O_3 by hydrogen bonding. The phenomenon confirmed that the surface of Al_2O_3 was coated with fluid molecule. The peak at 1392cm^{-1} was due to –CH_3 and indicated the presence of ethanol. The structure simulation diagram of Al_2O_3 in supercritical ethanol was showed in Fig. 3.

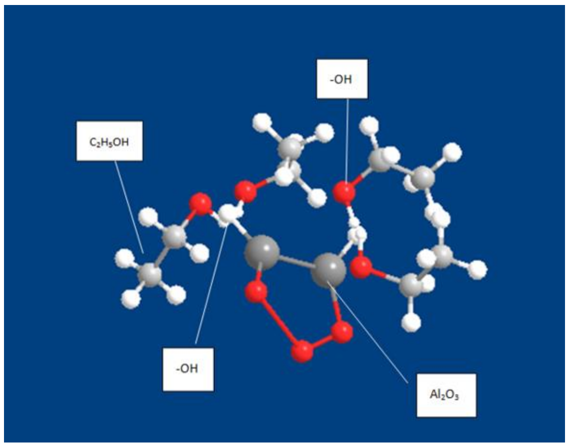


Fig. 3. The structure simulation diagram of Al_2O_3 in supercritical ethanol.

3.2 TEM analysis

The Al_2O_3 modified by supercutical fluid was investigated by TEM in order to observe the morphology and verified the result of FT-IR. Fig. 4 showed the TEM photographs and the energy spectrum analysis diagram of Al_2O_3 modified by supercutical fluid.

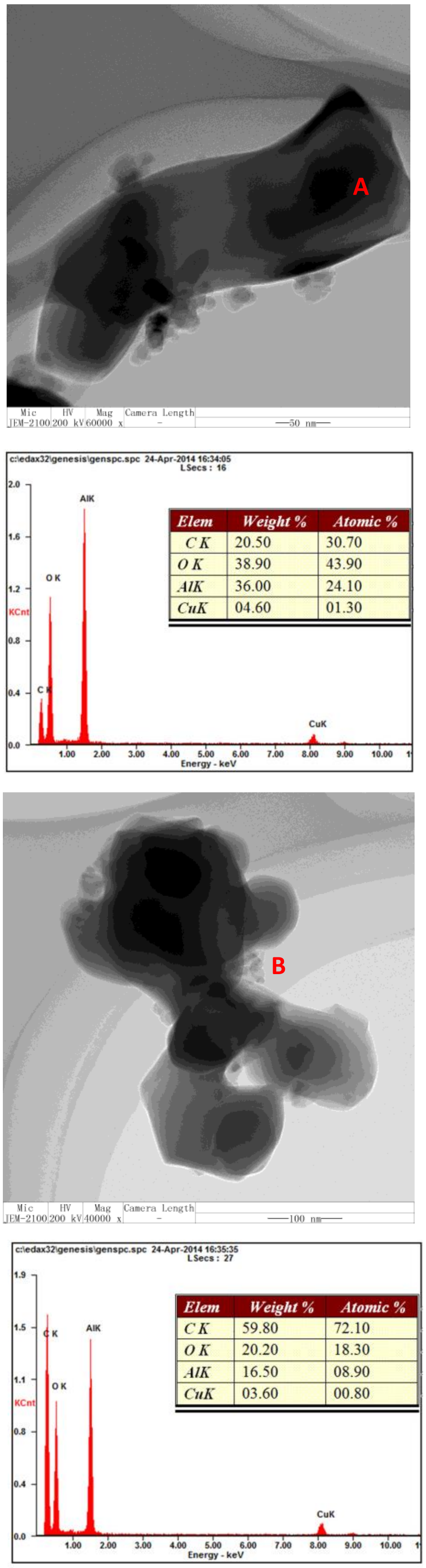
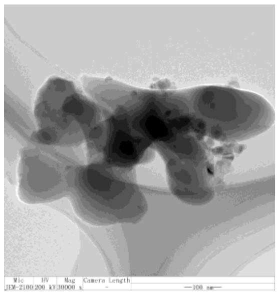
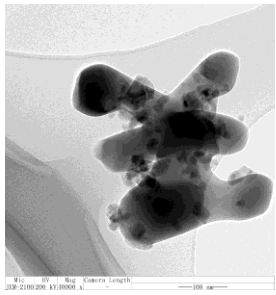


Fig. 4. TEM photographs and the energy spectrum analysis diagram of Al_2O_3 modified by supercritical fluid: (a) water and (b) ethanol.

Aluminum element was detected according the energy spectrum analysis of point A in Fig. 4 and the content was 36wt%, which was different from the content calculated by the molecule of Al_2O_3(52.9wt%). This was because the surface of Al_2O_3 was coated with carbon film, and the hydroxy formed when the surface of Al_2O_3 absorbed water. A point was Al_2O_3 particles according to Fig. 4. Carbon content of B point was higher than that of A point, oxygenium content was 20.2wt% and aluminum was 16.5wt%, and B point could be confirmed as ethanol molecule according to the composition of the test sample. The results of Fig. 4 indicated that the surface of Al_2O_3 would be coated with ethanol molecule, and the size of Al_2O_3 particles was about 30 nm which was identified with purchase specification.

Al_2O_3 modified by different fluid and under different processing time was also investigated by TEM, and Fig. 5 was the TEM photograph of Al_2O_3 modified by different fluid and under different processing time.





(a):*SCE*- Al_2O_3, 5min (b): *SCE*- Al_2O_3, 20min

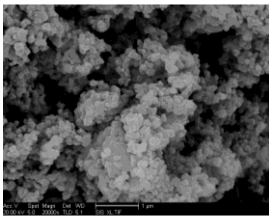
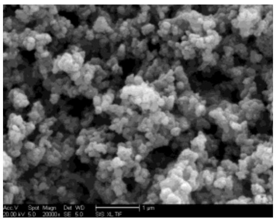
(c): *SCW*- Al_2O_3, 5min

Fig. 5. TEM photographs of Al_2O_3.

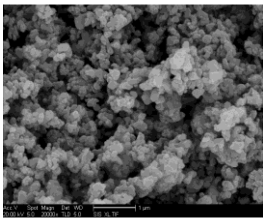
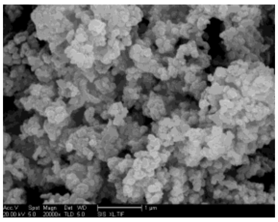
Fig. 5 suggested that the surface of Al_2O_3 modified by supercritical fluid was adhered by fluid molecule and the morphologies were different under different fluid and processing time. The coating amount increased while processing time extended, in Fig. 5 (a) and Fig. 5 (b), and the increasing of coating amount resulted in the reunion between Al_2O_3 particles. Fig. 5 (b) indicated that stack structure formed and led the effect of surface modification to become worse, when processing time extended. The reason was that the hydrogen bond between the molecules of fluid became weak, the structure was loose and polarity between fluid molecules declined, while the fluid was in the supercritical state, and the fluid molecules combined with Al_2O_3 through hydrogen bond [8]. The results of TEM comfirmed the result of FT-IR and the structure simulation diagram of Al_2O_3 in supercritical ethanol. The surface of Al_2O_3 modified by supercritical water was coated with fewer water molecules compared Fig. 5 (b) and Fig. 5(c), this was due to the polarity and hydrogen bonding of water.

3.3 SEM analysis

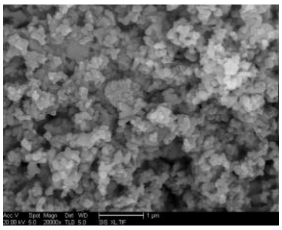
Pure-Al_2O_3 and modified by supercritical ethanol in different processing time (5min,15min and 20min) were measured by SEM, Fig. 6 was the SEM photographs of Al_2O_3.

(a) *pure*-Al_2O_3 (b) 5min *SCE*- Al_2O_3

(c) 15min *SCE*- Al_2O_3 (d) 20min *SCE*-Al_2O_3



(e) 5min *SCW*- Al_2O_3

Fig. 6. SEM photographs of Al_2O_3.

Fig. 6 showed that all of Al_2O_3 particles reached nano-scale. It could be seen that *pure*-Al_2O_3 existed in reunion state and emerged irregular shape in Fig.6 (a), and individual particle could not be found easily. This was because the surface of *pure*-Al_2O_3 was rich in hydroxyl and the hydrogen bond formed between hydroxyl, so, resulted in reunion [9-11]. The outline of nano-Al_2O_3 modified by supercrtical fluid was clear and the interaction between particles abated, the dispersion of particles was relatively uniform and loose. The effect of surface modification became worse while the processing time rose, compared Fig. 6 (a), (b) and (c). The coating amount increased with the increasing of processing time on the basis of the result of TEM and FTIR. The increasing of coating amount was not beneficial to the effect of surface modification. The surface modification effect of supercritical ethanol was better than that of supercritical water, because the polarity and hydrogen bonding of water was higher than that of supercritical ethanol. The water molecule could not adhere to the surface of Al_2O_3 and led the effect of surface modification to bad.

3.4 Dispersion and sediment measurement

Van der Waals force between the particles was much larger than its own weight in that the size of nano particle was below 100 nm [12-13], and such particle could keep suspending in the solution, would not subside quickly by gravity. But settling velocity of particle would become faster while reunion occurred. The dispersion and sediment measurement was occurred in liquid paraffin. Fig. 7 was the dispersion effect of particles in liquid paraffin and Table 1 was sediment volume of nano-Al_2O_3 particles for 24h. “V” and “t” represented sediment volume time, respectively.

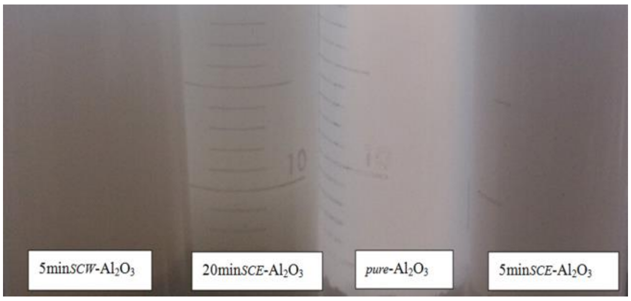


Fig. 7. Dispersion effect of particles in liquid paraffin.

Liquid paraffin was colorless transparent liquid and non-polar, Al_2O_3 particle was white and polar. *Pure*-Al_2O_3 could not disperse in liquid paraffin uniformly according the principle of the dissolution in the similar material structure. The mixture would become turbid liquid and was opaque, while the Al_2O_3 dispersed well. Al_2O_3 particle would pile up below the solution due to own gravity, and the translucency of upper mixture became well because the content of Al_2O_3 was low, while the Al_2O_3 could not disperse well. The better the translucency of mixture was, the worse the dispersity showed, therefore. As showed in Fig. 7, translucency of *pure*-Al_2O_3 was the best in all of samples, 5min *SCE*-Al_2O_3 was the worst. The polarity of nano-Al_2O_3 declined and could disperse in liquid paraffin uniformly due to the interaction between the hydroxyl of nano-Al_2O_3 and fluid molecules, while nano-Al_2O_3 was modified by supercritical fluid. The result of dispersion measurement suggested that the modified effect of 5min *SCE*-Al_2O_3 was the best, which kept with the results of TEM and SEM.

Table 1. The relation between settling volume and time.

Sample \ V/mL \ t/h	0	1	2	3	6	8	24
Al_2O_3	20.0	12.0	8.3	7.0	6.6	5.9	4.1
5min *SCE*-Al_2O_3	20.0	19.8	18.4	18.1	17.0	16.5	13.0
20min *SCE*-Al_2O_3	20.0	19.0	18.0	17.2	16.0	13.0	9.0
SCW-Al_2O_3	20.0	18.0	17.8	17.0	15.5	10.5	7.1

It could be seen from Table 1 that the particles of *pure*-Al_2O_3 settled qucikly in liquid paraffin, sediment volume reached 12ml after 1h. Since the superficial area of Al_2O_3 was large and surface energy was huge, reunion occurred easily. Gravity was greater than the van der Waals force in liquid paraffin, large particle settled quickly and carried small particle. The surface of Al_2O_3 was coated with ethanol molecule and the interaction between particles abated. The van der Waals force counterbalanced to gravity while the size of particle was below 10μm. The particles in liquid paraffin kept suspension state and formed loose deposition and the deposition would not settle quickly by gravity [14-15]. The settling volume of 5min *SCE*-Al_2O_3 was the highest, 20min *SCE*-Al_2O_3 was secondly and then *SCW*-Al_2O_3. This phenomenon was accordance with the results of FTIR, TEM and SEM. Table 1 manifested that the effect of surface modification of Al_2O_3 by supercrtical ethanol was better than that of supercrtical water, and became worse while the processing time rose.

4. Conclusions

The method of using supercritical fluid to modify nano-Al_2O_3 was effective and the mechanism between supercritical fluid and nano-Al_2O_3 was that the hydrogen bond between the molecules of fluid became attenuating while the fluid was in the supercritical state, the surface of nano-Al_2O_3 was coated with fluid molecules through the bonding between the hydroxyl of nano-Al_2O_3 and fluid molecules, and purpose of surface modification of nano-Al_2O_3 achieved. The effect of surface modification of nano-Al_2O_3 was best when the nano-Al_2O_3 was modified by supercritical ethanol and the processing time was 5min.

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