Preparation of Alumina Powder with Special Morphology

MA Chicheng, ZHOU Xuexi, ZHU Tun
Institute of Chemical Metallurgy, Chinese Academy of Sciences
Beijing, 100080 China

Synthesis of ammonium aluminum hydrogen carbonate(AAHC) via reaction of aluminum bicarbonate and aluminum salt and thermal decomposition is one of the important processes for preparation of high pure and ultra fine alumina. Kato and coworkers[1] developed this process, at same time Von Erdos and Altorfe[2] found AAHC in the corrosive products of aluminum in the atmosphere of carbon dioxide and ammonia. Murase and Iga[3] synthesized acicular AAHC in a autoclave under 60 to 120 ℃. Hayashi[4] optimized the conditions for preparation of AAHC and alumina.

Attempt has been made in this paper to reveal the conditions affect the morphology of the synthesized AAHC and the consequently produced alumina.

Experimental

Synthesis of AAHC was carried out in a reactor with mechanical stirrer and temperature controller. Aging of synthesised products was conducted in a 45mL Taflon lined stainless steel autoclave with a magnetic stirrer mounted in a temperature controlled heater. Solution of ammonium hydrogen carbonate and aluminum sulfate were reacted and then aged at different temperature, concentration, and pH value. Crystal and morphology of AAHC was examined by using TEM, XRD, IR, TDA and TGA,

Results and Discussion

Effect of Solution pH and Composition

Since dissociation of ammonium carbonate and the hydrolysis of aluminum ions depend on solution pH value, therefore pH also remarkably affects the formation and aging reaction of AAHC and the composition, consequently the particle size and morphology of the product. AAHC is preferentially formed in a higher molar ratio of NH_4HCO_3 to Al^{3+}, but the solubility of AAHC is very low, therefore, the formation reaction is always taken place in a high supersaturated solution and resulting in a very fine crystalline grain. AAHC prepared at different conditions mostly is spherecal particle composed with many smaller primary crystal. In order to produce grosser crystal, it is necessary to proceed aging process, in which smaller crystals are dissolving and larger ones are growing. Adding some ions in aging solution may causes the crystal growing in some direction quicker than other, then resulting in crystals and particle with special morphology.

Aging at a pH<7 with an additional aluminum ions, flocculent to hair-like particles were obtained, which means crystal grew quicker along the longitudinal direction than the diameter. Addition of ammonia to the aging solution to adjust to a pH>7 and mean while increased ammonium ions concentration and aging in a higher temperature resulted in acicular to bar-shaped particles with a much smaller ratio of longitude to diameter than that aged in lower pH solution.

Effect of Temperature and Time

Raising temperature increases the solubility of AAHC and accelerates the rate of dissolution and growth of crystal, results showed that as pH>7, higher the reaction and aging temperature produced particle with a larger size and a smaller ratio of longitude to diameter. Aging at a hydrothermal condition with a temperature of 100℃ for 48h strong bar-shaped particles is obtained. The effect of time is obvious, generally longer aging time larger particle is produced.

Composition of Particle

The photograph taken with a high resolution electronic microscope demonstrates that although the particles were aged for long time, the particles were composed of many micro-crystal grains integrated together. The boundary of the micro-crystal grains are clear and no any solid and liquid material in between the grains. The size of the micro-grain is about from 7 to 10nm. The distance between two lines in the image, which reflects the dimensions of the crystal lattices in certain direction, is estimated as 2.59 and 2.90A in the crystal and approximating to the distance between (221) and (220), respectively.

Structure of The Crystal

Erdos and Altorfe[2] reported the formula of the compound they obtained was $NH_4AlO(OH)HCO \cdot H_2O$ which is adopted by the JCPDS(ASTM)'s Standard XRD card, but Kato and coworkers[1] reported a composition $NH_4AlO(OH)HCO_3$, without the crystal H_2O. The XRD pattern and cell parameters determined by the two different groups were the same. This fact has been neglected by most literature, because only the formula, $NH_4AlO(OH)HCO_3$ has been mentioned in the papers came out afterwards.

Thermal Decomposition of AAHC

AAHC decomposed to aluminum oxide with the emission of NH_3, H_2O

and CO_2 under heating. Thermal gravity result of a sample aged at pH 8.2 weighted 8.83g revealed that the compound started decomposition at a temperature about 148℃, up to 800℃ the total weight loss was 6.48g, equal to 63.50% of the initial sample.

As $NH_4AlO(OH)HCO_3$ becoming Al_2O_3 the theoretical weight loss is 63.28%. The XRD pattern obtained in the laboratory is the same as reported by Kato[1], then the above result suggests the composition of the sample is $NH_4AlO(OH)HCO_3$. A sample aged at pH = 5.6 had a higher weight loss than the former one, and approximate to the formula, $NH_4AlO(OH)HCO_3 \cdot H_2O$, but the XRD pattern of this sample was the same as the former one, only the peaks were lower. It is demonstrates that the two samples in fact are the same compound, but the particles formed in lower pH had a even smaller size than that aged at a higher pH, and might capsule a litter water between the particles.

Decomposition was observed in a transmission electronic microscope with a heating sample holder, photographs of the morphology of particles were taken from room temperature up to 750℃. The pictures of different temperature showed that as decomposition of AAHC to alumina, although the weight loss was as high as 64%, the size and morphology had no obvious change. It is supposed that gradually emission of gases from the lattices did not cause remarkable change in the essential structure constructed by coordinated Al-O octahedrons.

As an AAHC sample with a specific surface area of $94.0m^2/g$ was heated at 600℃ for 5h to completely transfer to $\gamma-Al_2O_3$, the specific surface area of the produced alumina was $190m^2/g$. As thermal decomposition at a lower temperature and for a shorter time, higher specific surface area alumina has been obtained. Emission of gases from the crystal results in a lot of vacancy among the Al-O octahedron and increased the surface area.

References

1. S.Kato, T.Iga, S.Hatano, and Y.Isawa, Yogyo Kyokai Shi, 1976, 84(5):215-220.
2. Von E. Erdos and H.Altrofer, Werkstoffe und Korrosion, 1976, 27:611-618.
3. Y.Murase and T.Iga, Yogyo Kyokai Shi, 1987, 95(5):96-98.
4. K. Hayashi, J. Cer. Soc. Japan, 1990, 98:475-462.