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PREPARATION OF RUTILE POWDERS BY VAPOR PHASE REACTION OF $TiCl_4$-H_2-CO_2 SYSTEM

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Titanium dioxide powders of 98 % rutile content were obtained by vapor phase reaction of $TiCl_4$-H_2-CO_2 system at temperatures above 1000 °C. The average particle sizes of products were 0.11~0.66 μ. The sizes decreased with increasing reaction temperatures.

Introduction

TiO_2 produced by the chloride process is in the form of either anatase, rutile or their mixture depending on the reaction conditions. Rutile TiO_2 is more desirable because of its superior pigmentary characteristics and there are many patents concerning the control of the crystal form in the chloride process, in which $TiCl_4$ is either oxidized or hydrolyzed at temperatures between 1000° and 1400 °C in the presence of some nucleating agents, such as $AlCl_3$.[1)2)]

In this work, the vapor phase reaction of $TiCl_4$-H_2-CO_2 system was found to give 98 % rutile TiO_2 without additives.

Experimental

$TiCl_4$ from Ishizu Pharmaceutical Co., Ltd. was used.[3)] The mixture of CO_2 and H_2 was deoxidized by an activated Cu column and dried by a dry ice-ethanol trap. A mullite tube (28 mm I.D.) was used as a reaction tube. The H_2-CO_2 mixture saturated with $TiCl_4$ was injected into the reaction zone at 800 °C through a small mullite tube (4 mm I.D.). The products were collected in a flask at the end of the reaction tube.

Results and Discussion

Table 1 shows the reaction conditions and the properties of the products. The results with $TiCl_4$-H_2O system are also listed in Table 1 for comparison.

The product by the reaction at 900 °C was black titanium suboxide. This suboxide could be oxidized into white rutile by heating in air at temperatures between 260° and 530 °C (weight increase by oxidation: 2.8 %). The products produced at temperatures above 1000 °C were titanium dioxide and rutile contents were about 98 %. The product at 1000 °C, however, had a detectable deficiency of oxygen (weight increase by oxidation: 0.1 %) and was colored in gray. No weight increase by heating in air could be detected with the products at 1100° and 1205 °C. It has been observed that rutile content of TiO_2 powders from $TiCl_4$-O_2 system increases to appreciable extent, only when the reaction gases are injected into the high-temperature reaction zone

Table 1. Reaction conditions and properties of products.

Run	Reaction temperature (°C)	Gas composition[a] $TiCl_4$ (%)	CO_2 (%)	H_2 (%)	Color	Wr[b] (wt%)	Lattice const.[c] a_o (Å) (±0.002)	c_o (Å) (±0.002)
1	900	3.4	51.7	44.9	black	-	-	-
2	1000	3.4	51.7	44.9	gray	98	4.600	2.955
3	1100	3.4	51.7	44.9	white	98	4.598	2.959
4	1205	3.4	51.7	44.9	white	97	4.595	2.960
$TiCl_4$-H_2O system								
6[d]	1100	1.4	(H_2O) 1.7		white	38	4.596	2.959

a) Total flow rate: 200 ml/min b) Rutile content by Spurr's method.[4]

c) Values in ASTM card no.4-0551: a_o = 4.594 Å, c_o = 2.958 Å.

d) $TiCl_4$ and H_2O were mixed at 1050 °C by using nitrogen as a carrier gas.

above 900 °C and that rutile content was only 20 to 40 % even at 1100 °C.[5)6)]

The formation reactions of TiO_2 from $TiCl_4$-H_2-CO_2 system can be represented as:

$$CO_2 + H_2 = H_2O + CO \quad (1) \quad \text{and} \quad TiCl_4 + 2H_2O = TiO_2 + 4HCl \quad (2)$$

Table 1 shows that rutile content of TiO_2 from $TiCl_4$-H_2O system (eq.(2)) is 38 %. Therefore, the high rutile content of TiO_2 from $TiCl_4$-H_2-CO_2 system may be related to the existence of H_2. The mechanism of the hydrogen effect is in investigation.

The electron micrographs showed that TiO_2 particles from $TiCl_4$-H_2-CO_2 system were nearly spherical with the average particle sizes about 0.66, 0.20 and 0.11 μ at 1000°, 1100° and 1205 °C, respectively. The most suitable particle size for TiO_2 powders as pigment is 0.2~0.3 μ. It seems that the particle sizes of TiO_2 powders from $TiCl_4$-H_2-CO_2 system can be controlled by the reaction conditions.

References and Note

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3) Purity is 99.99 %. Impurities: sulfate < 0.003 %, heavy metals < 0.001 % and iron < 0.0005 %.

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