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FORMATION OF TITANIC OXIDES OF ANATASE, BROOKITE AND RUTILE TYPES BY AERIAL OXIDATION OF TITANOUS SOLUTIONS

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Aerial oxidation of titanous solutions has been carried out at temperatures between 60° and 95°C. A desired one of titanic oxides of anatase, brookite and rutile types, can be obtained from strongly acidic solutions by selection of the kind and concentration of anions present and temperature.

Titanic oxide, TiO_2, can be obtained not only by calcination of titanic compounds but also by precipitation in aqueous solutions of titanic salts. The precipitation in the solutions has long been studied. According to these studies, two modifications of titanic oxide, anatase and rutile types, can be precipitated by hydrolysis of the acidic solutions and their formation depends on the kind of anions present, temperature, etc.[1)~3)]

In order to clarify the nature of transition metal oxides, we(M. K. and T. T.) have long studied the formation of many oxides in aqueous solutions and suspensions. They were precipitated by hydrolysis and oxidation. By oxidation more modifications of the oxides were obtained than by hydrolysis. For example, slow oxidation of titanous salt solutions caused the formation of titanic oxides of anatase, brookite and rutile types. In this letter the conditions for the formation of each oxide will be reported.

Experimental and results

The titanous chloride solution used as the starting material was obtained from Wako Pure Chemical Industries, Ltd. This solution contained 2.0M in $TiCl_3$, 1.6M in $ZnCl_2$ and 1.2M in HCl.

To NaOH solution the titanous chloride solution was added in the ratios of NaOH to all Cl^- ions in it of 0.65, 1.0 and 1.2 equivalent and was diluted with

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Table 1. Kind of TiO_2 obtained by aerial oxidation of strongly acidic solutions.

No	Conditions			TiO_2 obtained
	Starting solution*		Temp.	
	M in $TiCl_3$	M in Na salt	(°C)	
1	0.166		60	Rutile
2	0.166		95	Rutile, Brookite
3	0.033		95	Brookite
4	0.333		95	Rutile
5	0.166	0.166(Na_2SO_4)	95	Anatase
6	0.166	0.166(CH_3COONa)	95	Brookite

*$ZnCl_2$ and excess HCl in it are omitted.

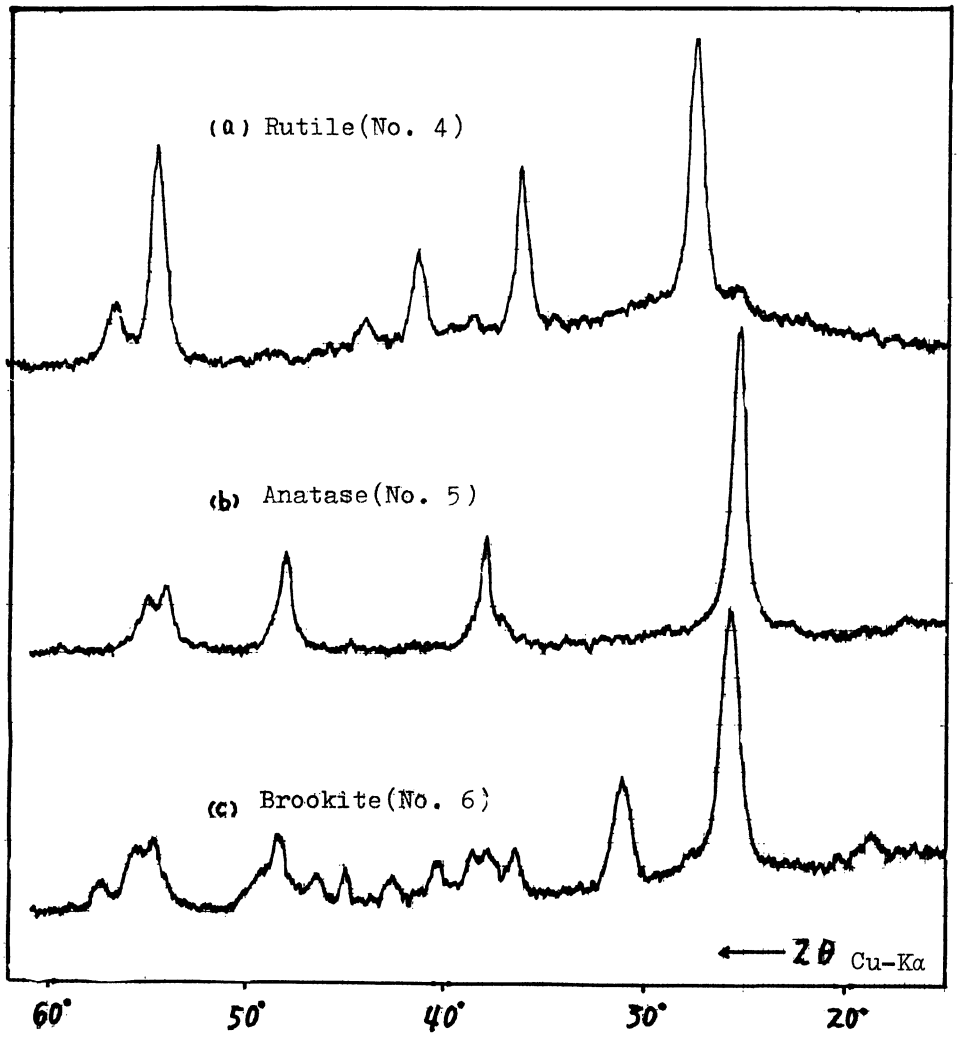

Fig. 1. X-ray diffraction patterns of titanic oxides.

water to 0.166M in Ti ion. Suspensions of titanous precipitates thus prepared were oxidized at 95°C by flowing the air into them at the rate of 200 l/hr. As the oxidation progressed, their color gradually changed from black to white. After 20 hr, the white precipitates were filtered, washed with water and then dried at about 100°C. The samples thus obtained were examined by X-ray diffraction method using Cu-Kα radiation. The sample obtained from the suspension with the $NaOH/Cl^-$ ratio of 0.65 was a mixture of TiO_2 of brookite type and that of rutile type and the other samples were amorphous. This may indicate that an increase in the acidity favorably affected the formation of TiO_2.

In order to examine the effects of the concentration and kind of the anions in strongly acidic solutions and temperature on the formation of modifications of TiO_2, the following experiments were carried out. Strongly acidic solutions with different concentrations of $TiCl_3$ were prepared by dissolving the titanous chloride solution into water. Also mixture of the titanous chloride solution and one of Na_2SO_4, CH_3COONa, $NaNO_3$ or $NaClO_4$ solution (which contained 0.166M in $TiCl_3$ and 0.166M in the salt) was prepared. The solutions thus prepared were subjected at temperatures between 60°and 95°C to the same oxidation as above. TiO_2 of anatase, brookite or rutile type or their mixture could be obtained by selection of the kind and concentration of the anions, and temperature. The typically experimental conditions for forming the modifications of TiO_2 are given in Table 1. Their typical X-ray diffraction patterns are shown in Fig. 1.

The oxidation of strongly acidic chloride solution results in the formation of either rutile or brookite type, or their mixture, depending on the concentration of the chloride and temperature. TiO_2 of anatase type was precipitated at temperatures between 60°and 95°C in the solution containing the sulphate. The addition of the acetate to the chloride solution favorably affects the formation of TiO_2 of brookite type. The solubility product of $[Zn^{2+}][OH^-]$ is about 10^{-18}. The titanic oxides contained the least amount of Zn ion (below 0.5 wt%). When $NaNO_3$ and $NaClO_4$ solutions were added to the acidic solution, their color quickly changed from dark blue to colorless and white precipitates were gradually formed. These precipitates could not be separated from the solution by filtration because their particle size was very small.

When an acidic solution of titanous cholride in which no Zn ion was present was used as the starting material, these three modifications were obtained by the selection of conditions.

We believe that their formation is closely connected with the nature of titanium ions in the solution before the formation of the precipitates.

References

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