Formation of Zinc Oxide by Homogeneous Precipitation Method

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Synopsis. The process of ZnO formation depends on the concentration of $ZnCl_2$ and the $(CH_2)_6N_4/ZnCl_2$ molar ratio(R), and there are two routes leading to ZnO: One is its direct formation, and the other is via $Zn_5Cl_2(OH)_8$ as an intermediate.

Solution-phase ZnO preparation is generally carried out by mixing $Zn(OH)_2$, obtained by adding an alkaline solution to a zinc salt solution, with a mother liquid followed by boiling for several hours.[1,2] This process, however, is featured by poor reproducibility regarding the particle shape and size of ZnO prepared. A homogeneous precipitation method leads to a homogeneous precipitate with good reproducibility in composition and properties.[3,4] Though we previously described the preparation of ZnO by the homogeneous precipitation method,[5] the conditions for its direct formation by this method has not been reported. Hexamethylenetetramine (HMTA) in the aqueous solution hydrolyzes to produce ammonia and formaldehyde in the course of heat treatment.[6] The concentration of HMTA affects the rate of ZnO formation and the structure of the complex ion with Zn^{2+}.[7] In view of this, we prepared ZnO by varying the concentration of $ZnCl_2$, the $(CH_2)_6N_4/ZnCl_2$ molar ratio, and the heating time, to examine the possibility of direct ZnO formation by the homogeneous precipitation method.

Experimental

Hydrochloric acid (0.01 mol dm^{-3}) was used as a solvent to keep the aqueous solution of $ZnCl_2$ strongly acidic. An aqueous solution (1 dm^3) containing $ZnCl_2$ (0.01 to 0.08 mol dm^{-3}) and HMTA (molar ratio R=0.2 to 20) was heated at 95—97 °C in a steam bath for 15—60 min. $Zn_5Cl_2(OH)_8$ was prepared from the aqueous solution (1 dm^3) containing both $ZnCl_2$ (0.1 mol dm^{-3}) and HMTA (0.02 mol dm^{-3}) heated at 95—97 °C in a steam bath for 60 min. To a solution containing NH_4Cl (0 to 0.05 mol dm^{-3}) and HCHO (0 to 1.0 mol dm^{-3}), 0.3 g of $Zn_5Cl_2(OH)_8$ was added to form a suspension. The suspension (0.1 dm^3) was heated at 95—97 °C in a steam bath for 15—60 min. The precipitate was filtered, washed with distilled water, and dried under vacuum at room temperature. All of the chemicals used in this experiment were of analytical grade from Wako Pure Chemicals Co., Ltd. X-Ray diffraction analysis was carried out with an X-ray diffractometer (Rigaku RAD-C). The ZnO particle shape and diameter were examined under a microscope (Olympus BHS-RFK).

Results and Discussion

Table 1 shows the relationship between the nature of the product and the $ZnCl_2$ concentration, for two $(CH_2)_6N_4/ZnCl_2$ molar ratios (R=0.2 and 1.0). No precipitation was noted when the $ZnCl_2$ concentration was 0.01 mol dm^{-3}. When the $ZnCl_2$ concentration was 0.02 mol dm^{-3} and the molar ratio R was 0.2, ZnO was precipitated by heating for 30 min but not by heating for 15 min. An increase in the R value to 1.0 resulted in the precipitation by heating for 15 min. The products were ZnO and $Zn_5Cl_2(OH)_8$ at lower (0.02 and 0.03 mol dm^{-3}) and higher (0.05—0.08 mol dm^{-3}) $ZnCl_2$ concentrations. Both ZnO and $Zn_5Cl_2(OH)_8$ was produced at the concentration of 0.04 mol dm^{-3}. For each $ZnCl_2$ concentration, the product was common for the two R values. These results show that the $ZnCl_2$ concentration and the R value exert an effect on the induction period and on the nature of the product.

Table 1. Effects of $ZnCl_2$ Concentration and $(CH_2)_6N_4/ZnCl_2$ Molar Ratio on the Product Distribution

$ZnCl_2$	R	
mol dm^{-3}	0.2	1.0
0.01	—	—
0.02	Z	Z
0.03	Z	Z
0.04	Z,B	Z,B
0.05	B	B
0.06	B	B
0.07	B	B
0.08	B	B

Z: ZnO, B: $Zn_5Cl_2(OH)_8$, —: no precipitation, R=$(CH_2)_6N_4/ZnCl_2$ molar ratio.
Solutions of R=0.2 and 1.0 were heated for 30 and 15 min, respectively.

Figure 1 shows the effects of the reaction time, the $ZnCl_2$ concentration and the R value on the product of the solution-phase reaction. The X-ray diffraction intensity was taken as a measure of the amount of the compound in question. At low $ZnCl_2$ concentration (0.01 mol dm^{-3}), ZnO was formed rapidly regardless of the R value (2 and 20). At high $ZnCl_2$ concentration (0.1 mol dm^{-3}) and small R (0.2), $Zn_5Cl_2(OH)_8$ was produced in a short period. For these two cases the amounts of the products remained constant. In contrast, at a $ZnCl_2$ concentration of 0.05 mol dm^{-3} and R=2, both ZnO and $Zn_5Cl_2(OH)_8$ were formed in an early stage of the reaction, and the former tended to increase while the latter tended to decrease as the reaction proceeded. This shows that the initial product $Zn_5Cl_2(OH)_8$ is converted into ZnO in the course of aging in the mother liquor. The particle sizes of ZnO produced at a $ZnCl_2$ concentration of 0.01 mol dm^{-3} were about 5 μm (needle shape) and about 1 μm (globular shape) for R=2 and 20, respectively.

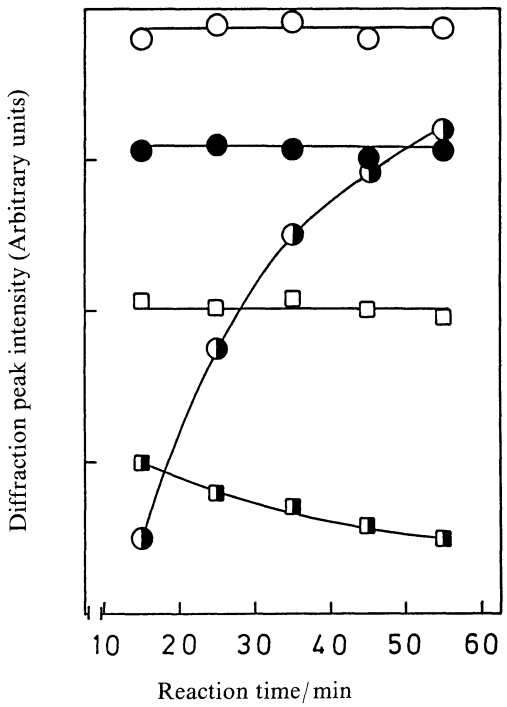

Fig. 1. Effects of $ZnCl_2$ concentration, $(CH_2)_6N_4/ZnCl_2$ molar ratio, and the reaction time on the X-ray diffraction intensities of ZnO and $Zn_5Cl_2(OH)_8$. Conditions: $ZnCl_2$ concentration and the molar ratio $R=(CH_2)_6N_4/ZnCl_2$. ○, ●: 0.01 mol dm^{-3}, R=2 and R=20, □: 0.1 mol dm^{-3}, R=0.2, ◑, ◨: 0.05 mol dm^{-3}, R=2, (○, ●, ◑): ZnO(100) plane, (□, ◨): $Zn_5Cl_2(OH)_8$(107) plane.

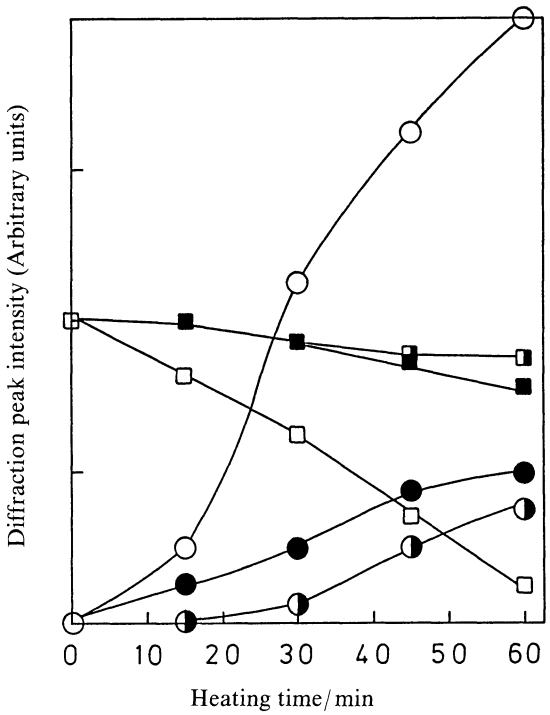

Fig. 2. Effects of solvent and heating time on the X-ray diffraction intensities of ZnO and $Zn_5Cl_2(OH)_8$. Solvents. ○, □: distilled water, ●, ■: with 0.01 mol dm^{-3} NH_4Cl, ◑, ◨: with 0.01 mol dm^{-3} NH_4Cl and 0.1 mol dm^{-3} HCHO, (○, ●, ◑,): ZnO(100) plane, (□, ■, ◨): $Zn_5Cl_2(OH)_8$(107) plane.

Hexamethylenetetramine hydrolyzes to generate ammonia and formaldehyde on heating.[6] When $Zn_5Cl_2(OH)_8$ changes into ZnO upon aging in a mother liquor, NH_4Cl and HCHO should be contained in the solution. In view of this, we examined the effect of the concentration of NH_4Cl (0—0.05 mol dm^{-3}) and HCHO (0—1.0 mol dm^{-3}) on the conversion of $Zn_5Cl_2(OH)_8$ into ZnO. A $Zn_5Cl_2(OH)_8$ suspension in a solution containing NH_4Cl and HCHO was heated at 95—97 °C in a steam bath for 60 min. The product distribution was not affected by the presence of HCHO. However, by addition of NH_4Cl at a concentration of 0—0.03 mol dm^{-3}, a mixture of ZnO and $Zn_5Cl_2(OH)_8$ was obtained. At a higher NH_4Cl concentration (0.05 mol dm^{-3}), $Zn_5Cl_2(OH)_8$ was the sole product. Figure 2 shows the time courses of the amounts of ZnO and of $Zn_5Cl_2(OH)_8$ for this conversion in distilled water, in a 0.01 mol dm^{-3} NH_4Cl solution, and in a solution containing both 0.01 mol dm^{-3} NH_4Cl and 0.1 mol dm^{-3} HCHO. An increase in the amount of ZnO is accompanied by a decrease in that of $Zn_5Cl_2(OH)_8$. At a given heating time, the amount of ZnO formes in a suspension without NH_4Cl is larger than that formed in a suspension containing NH_4Cl. These results indicate that NH_4Cl suppresses the conversion of $Zn_5Cl_2(OH)_8$ into ZnO. This in turn shows that the ZnO observed in the initial stage is a direct product of the reaction.

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