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THE EFFECT OF CHLORINE OR ITS COMPOUNDS ON THE REACTION OF η-Al_2O_3 WITH ZnO

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The addition of a small amount of chlorine or its compounds ($AlCl_3 \cdot 6H_2O$ and HCl) accelerated remarkably the reaction of η-Al_2O_3 with ZnO.

In general, it has been known that the reactivity of solids changes remarkably according to their preparation conditions. The authors have discussed the reactivity of transition aluminas, especially of η-Al_2O_3, for $ZnAl_2O_4$ formation, which were obtained by the thermal decomposition of various hydrous aluminum salts.1) It has been found that the reactivity of η-Al_2O_3 samples changes with their specific surface area and by the existence of impurity-anions remaining in η-Al_2O_3 after the thermal decomposition of aluminum salts. The purpose of this paper is to show the existence of a strong accelerating effect of chlorine or its compounds($AlCl_3 \cdot 6H_2O$ and HCl) on $ZnAl_2O_4$ formation.

The details of experimental techniques have been described in the previous papers.1),2) The samples of η-Al_2O_3 used in the experiments were prepared by the thermal decomposition of four hydrous aluminum salts, $Al_2(SO_4)_3 \cdot 18H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $AlCl_3 \cdot 6H_2O$ and $Al_2O(CH_3COO)_4 \cdot xH_2O$, in the stream of air (50 ml/min) at 850°C for 2 hr. The samples obtained from these salts are indicated hereafter by η-Al_2O_3(S), η-Al_2O_3(N), η-Al_2O_3(Cl) and η-Al_2O_3(Ac), respectively. ZnO was obtained by the thermal decomposition of basic zinc carbonate, $5ZnO \cdot 2CO_3 \cdot 4H_2O$, in air at 500°C for 30 min. All samples of η-Al_2O_3 and ZnO were ground to pass through 300 mesh sieve and mixed in equimolar ratio. The reaction was carried out at 650°C for various times in air. The fractional formation of $ZnAl_2O_4$(α) was calculated from the amount of unreacted ZnO.

Figure 1 shows the rate of $ZnAl_2O_4$ formation measured for four systems of η-Al_2O_3 – ZnO at 650°C, except for η-Al_2O_3(N) system where the reaction was carried out at 750°C (curve d). It is found that the reactivity of η-Al_2O_3 is in the following order; η-Al_2O_3(Cl) > η-Al_2O_3(S) > η-Al_2O_3(Ac) > η-Al_2O_3(N). The results in Fig.1 fitted to Jander's rate equation in which the rate constant, k_J, is represented by $k_J = 2kD/r_0^2 = k'D\rho^2S^2$, where k and k' are constant, r_0 particle size, ρ density, D diffusion constant and S specific surface area.1),2) The values of k_J at 650°C were 7.65×10^{-4} min^{-1} for η-Al_2O_3(Cl), 2.74×10^{-4} min^{-1} for η-Al_2O_3(S), 7.10×10^{-5} min^{-1} for η-Al_2O_3(Ac) and 3.54×10^{-5} min^{-1} for η-Al_2O_3(N) at 750°C. The effect of ρ^2 on k_J was small and was found to be neglected.3) Therefore, k_J depends on the product of D and S^2. The specific surface areas measured were 78 m^2/g for η-Al_2O_3(Cl), 169 m^2/g for η-Al_2O_3(S), 103 m^2/g for η-Al_2O_3(Ac) and 31 m^2/g for η-Al_2O_3(N). The order of reactivity shown above agrees with the order of the specific surface area(S) of η-Al_2O_3 except for η-Al_2O_3(Cl). On the other hand, although the value of S of

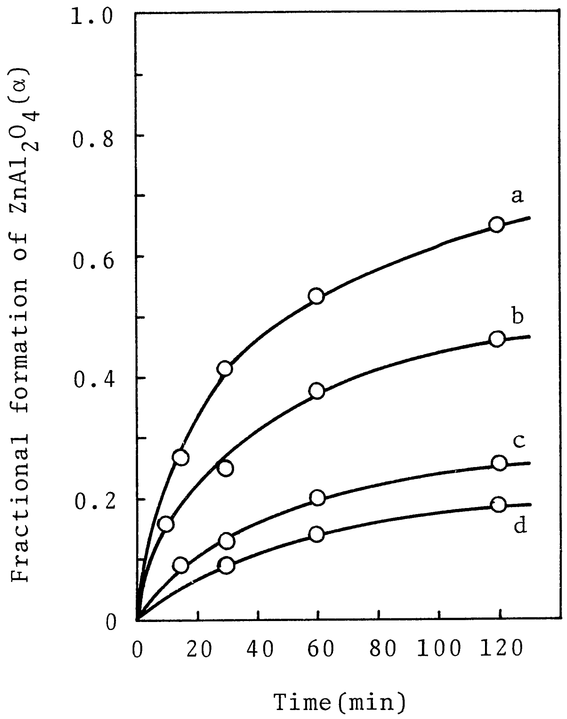

Fig.1 Rate of $ZnAl_2O_4$ formation at 650°C (a~c) and 750°C (d)

a: ZnO – η-Al_2O_3(Cl) system

b: ZnO – η-Al_2O_3(S) system

c: ZnO – η-Al_2O_3(Ac) system

d: ZnO – η-Al_2O_3(N) system

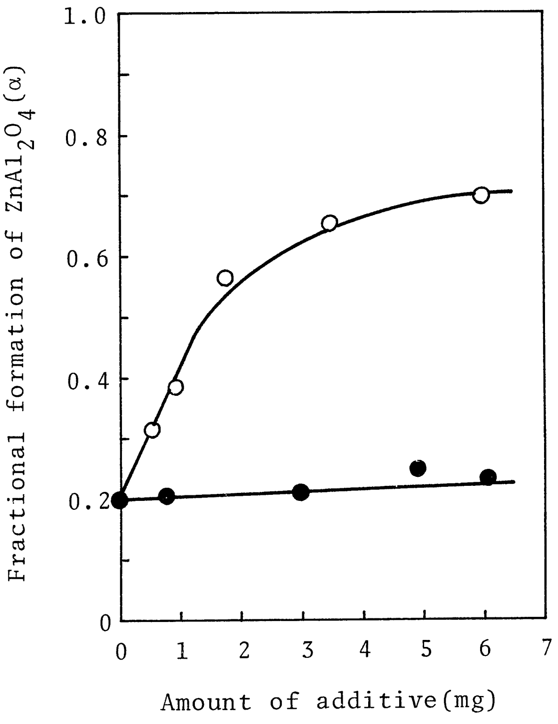

Fig.2 Effect of additives on the reaction of η-Al_2O_3(Ac) with ZnO at 650°C for 1 hr (Reactant, 50 mg)

-○-: addition of $AlCl_3\cdot6H_2O$

-●-: addition of $Al_2O(CH_3COO)_4\cdot xH_2O$

η-Al_2O_3(Cl) is small, its reactivity is highest. This fact results probably from an accelerating action of residual chlorine in η-Al_2O_3(Cl), i.e., an enough large value of D to compensate the small value of S. The existence of residual chlorine in η-Al_2O_3(Cl) was observed by the qualitative chemical analysis with silver nitrate solution.

Figure 2 shows the effect of addition of $AlCl_3 \cdot 6H_2O$ and $Al_2O(CH_3COO)_4 \cdot xH_2O$ on the reaction of ZnO with η-Al_2O_3(Ac) which is free from chlorine. The reaction was carried out at 650°C for 1 hr by using 50 mg of a equimolar mixture. The additives decomposed completely at this temperature. In the case of $Al_2O(CH_3COO)_4 \cdot xH_2O$, the values of fractional formation (α) of $ZnAl_2O_4$ change scarcely and are almost same value($\alpha = 0.2$) as that obtained without any additive. On the other hand, the addition of $AlCl_3 \cdot 6H_2O$ results in a remarkable increase in α-value with increasing amount of the additive. This behavior suggests the accelerating effect of Cl_2 or HCl evolved by the thermal decomposition of $AlCl_3 \cdot 6H_2O$.

Table 1. Effect of hydrogen halides on the reaction of η-Al_2O_3(Ac) with ZnO at 650°C for 1 hr

without additive	HCl	HBr	HF	HI	Cl_2
$\alpha = 0.20$	0.65	0.65	0.52	0.28	0.57

A few paper has been reported concerning the effect of Cl_2 or HCl on the solid -state reaction, e.g., the reaction of CaO with SiO_2,$^{4)}$ the thermal oxidation of silicon,$^{5)}$ and the fabrication of transparent polycrystalline MgO.$^{6)}$

Table 1 shows the effect of hydrogen halides (HCl, HBr, HF and HI) on the reaction of η-Al_2O_3(Ac) with ZnO. The acid (conc., 0.1 ml) taken in a porcelain boat was placed adjacently to another boat containing the sample in a quartz reaction tube. Both ends of the reaction tube were packed with asbestos. All acids vaporized at the reaction temperature. As seen in Table 1, the addition of HCl, HBr and HF increases α-value by a factor of about three times. On the other hand, the accelerating effect of HI is very small. Moreover, when Cl_2 gas (2 ml) is injected into the reaction tube, the fractional formation (α) also increases as much as the addition of

HCl. It is very interesting that the rate of $ZnAl_2O_4$ formation increases remarkably when η-Al_2O_3 contains a very small amount of chlorine, or chlorides ($AlCl_3 \cdot 6H_2O$ and HCl) are added to the reaction system of η-Al_2O_3 – ZnO.

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