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THE CRYSTALLITE SIZE OF α-IRON IN THE PRESENCE OF K_2O IN THE DOUBLY PROMOTED AMMONIA SYNTHESIS IRON CATALYSTS

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Besides the effect of electronic factor of K_2O in the doubly promoted ammonia synthesis iron catalysts, K_2O shows an another function to control a crystallite size of α-iron which is formed by reduction of the catalysts with hydrogen.

The promoter functions of alumina and potassium oxide in the ammonia synthesis iron catalysts have extensively been discussed in connection with the structural effects as well as the mechanism of the decomposition and the synthesis of ammonia.[1)-5)] The results so far obtained show that the oxide catalyst has a magnetite structure, and alumina goes into solid solution with magnetite, and it also prevents the sintering of α-iron particles formed by the reduction. However, very little has been known of the effect and location of potassium oxide in the magnetite phase as well as in the reduced state of the catalyst. In the present communication, we report the effect of potassium oxide to the crystallite size of α-iron in the doubly promoted catalyst, which was performed by X-ray diffractometry.

The catalysts used were identical with those used in the previous paper.[4)] The catalysts contain various amount of potassium oxide from 0 to 1.54 wt% (No.1; 0, No.2; 0.33, No.3; 0.58 and No.4; 1.54 wt%) with almost fixed concentration of alumina (ca. 2.5 wt%) and a small amount of silica as impurity besides iron oxide. The composition and surface characterization by adsorption method are shown in the previous paper.[4)]

The powdered catalysts of 44 μm in maximum size were reduced with a flowing hydrogen with high purity in an X-ray diffractometer. Initial reduction temperature was 300°C, and then it was increased stepwise to 350, 400 and finally 500°C. During the reduction, the X-ray diffraction patterns were observed at each temperature. Iron oxide completely disappeared from the pattern taken at 500°C. The crystallite dimension (D_{hkl} Å) of α-iron formed after the final reduction were evaluated from the diffraction peak-width by Scherrer's method. D_{hkl} were determined along the directions of <200>, <211>, and <220>.

Figure 1 shows the effect of K_2O contents in the unreduced catalysts to

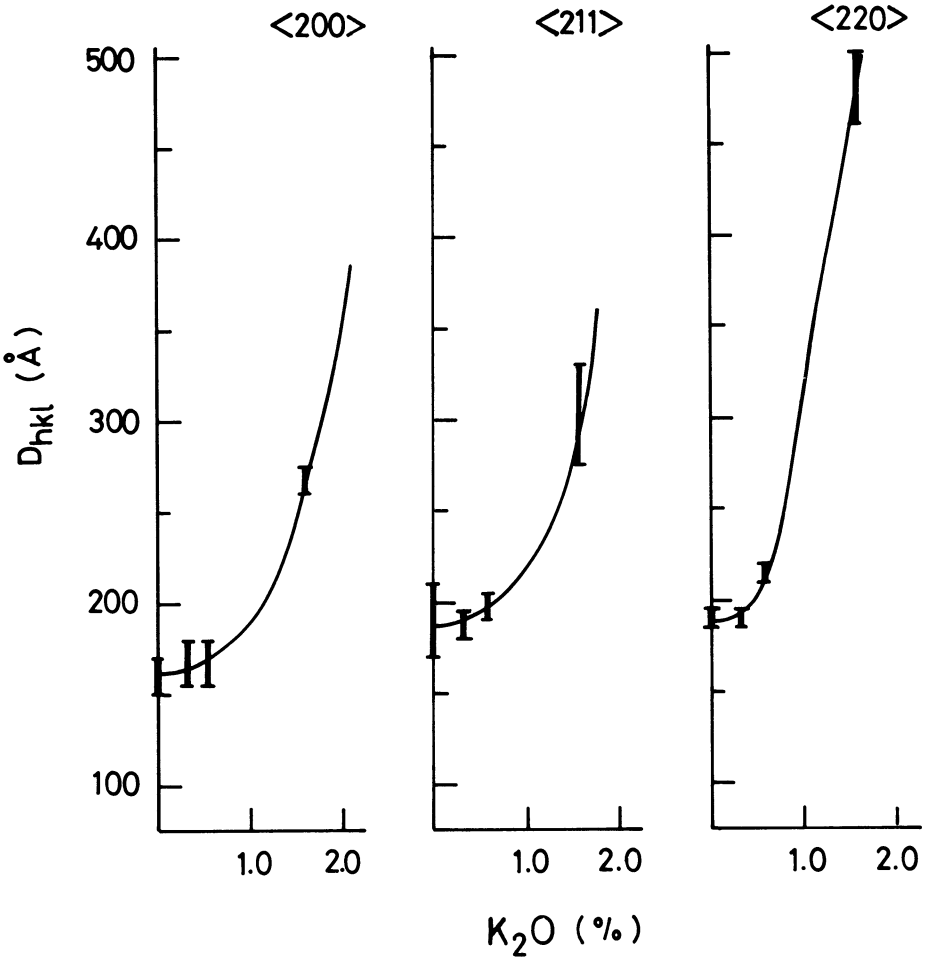

Fig. 1 The relation between the K_2O contents in the unreduced catalysts and the crystallite size of α-iron in the reduced catalysts at 500°C. Vertical bar shows the error accompanied by the measurements.

the crystallite size of α-iron which was formed with reduction at 500°C. In the range up to 0.58 % of K_2O (No.1~No.3), significant change in the crystallite size cannot be observed in any directions. Beyond 0.58 % of K_2O contents, the crystallite size increased significantly, which is agreed with the fact that the surface area of the reduced catalysts containing above 0.58 % of K_2O decreases smoothly at the higher reduction temperature.[4] This indicates that the addition of small amounts of K_2O also prevents the growth of the crystallite size.

The reasons for the growth of the crystallite size of α-iron with the increase of K_2O contents can be understood from the analysis of the observed diffraction patterns of the catalysts before reduction. The lattice constants of the magnetite phase in the catalysts with K_2O contents less than 0.58 % are the same within the experimental accuracy i.e. No.1; a_0 = 8.3786(6) Å, No.2; a_0 = 8.3782(7) Å, No.3; a_0 = 8.3784(8) Å, whereas the catalyst with excess K_2O, No.4, shows rather larger value (a_0 = 8.3821(6) Å) (figures in bracket show standard deviation). As is well known, alumina forms easily a solid solution with magnetite in which Fe^{3+} ions are replaced by Al^{3+} ions,[6)-8)] but the addition of K_2O prevents to some extent the formation of the solid solution.[9] This implies that alumina can be withdrawn from the solid solution in the presence of excess K_2O , because the lattice constants of the solid solution increase linearly with decrease of alumina contents in accordance with the Vegard's law.[6)-8)] Therefore, it can be said that amounts of alumina in the magnetite phase decrease with the increase of K_2O contents above 0.58 %. In fact, the catalyst No.4 contains traces of β-Al_2O_3, $K_2Fe_{22}O_{34}$ and unidentified phase before the reduction, whereas no such compounds except the last one are found in the other samples. The unidentified phase has the strongest peak at 17 Å of the interplaner spacings.

On the basis of the results obtained, it may be concluded that K_2O has an effect to control indirectly the crystallite size of α-iron formed by the reduction of the doubly promoted fused iron catalysts besides of its electronic factor. This function is due to that the excess amounts of K_2O withdraw the Al_2O_3 from the magnetite phase in the catalysts.

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