Change in the Structure of Evaporated Aluminum Chloride by Adsorbing Several Substances

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The catalytic polymerization of propylene on evaporated aluminum chloride has been studied in the absence of a solvent by spectroscopic methods and a kinetic method[1-4] in order to make clear the reaction mechanism.

During the course of these studies, it was found that the infrared spectrum of evaporated aluminum chloride is changed slowly by the adsorption of benzene derivatives, cyclohexene, and nitromethane. Therefore, infrared spectrum of crystallized aluminum chloride was measured for the sake of comparison and in order to make clear this phenomenon.

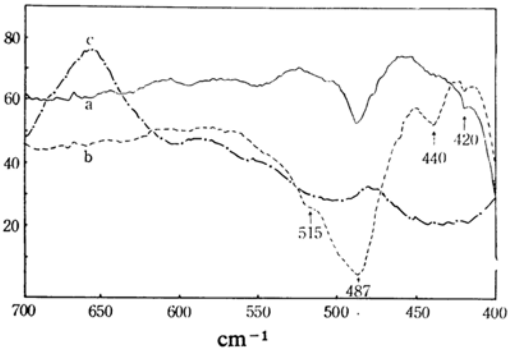

Fig. 1. Infrared absorption spectrum of evaporated aluminum chloride absorbing *p*-xylene.

a ——— Evaporated aluminum chloride alone
b ------ Evaporated aluminum chloride adsorbing *p*-xylene
c —·—· Crystallized aluminum chloride

In Fig. 1, curves a and b show a change in the infrared spectrum of evaporated aluminum chloride by adsorbing *p*-xylene. The band near 487 cm^{-1} increased remarkably in intensity and in width with the lapse of time. Furthermore, new bands were observed near 520—500, 440 and 420 cm^{-1}. Even if this system was evacuated until the infrared bands due to *p*-xylene vanished, these bands did not change. However, these bands did disappear upon the addition of water. The same phenomenon was also observed with the adsorption of benzene, toluene, mesitylene, cyclohexene, and nitromethane. On the other hand, the phenomenon was not observed in the case of the adsorption of nitrogen or cyclohexane.

Curve c shows the infrared spectrum of crystallized aluminum chloride, which can be observed by mixing aluminum chloride with Nujol, putting the mixture between two potassium bromide plates, and painting vacuum grease around the potassium bromide plates. This spectrum shows that very broad absorption bands exist near 600, 500 and 450—420 cm^{-1}. Aluminum chloride was recently evaporated onto a platinum plate at -195°C by Perkampus and Baumgarten,[5] who observed its reflective absorption spectrum. By annealing the evaporated aluminum chloride, they found that the bands near 606 (very strong) and 467 cm^{-1} (strong) shifted to a lower wavelength, i. e., 599 (very strong) and 440 cm^{-1} (very strong), while the 508 cm^{-1} band increased in intensity.

In view of this fact, the appearance of the infrared bands near 520—500 and 440 cm^{-1} may be due to the crystallization of the evaporated aluminum chloride. When aluminum chloride is evaporated onto a potassium bromide plate at room temperature, the band near 487 cm^{-1} increases remarkably in intensity. On the other hand, when aluminum chloride is evaporated onto the platinum plate at -196°C, the band does not even seem to exist, judging from the above data. This band was assigned by Klempeler to the dimer structure of gaseous aluminum chloride. This finding may suggest that the increase in the band near 487 cm^{-1} is due to the dispersed state of the evaporated aluminum chloride.

On the basis of these data, it seems reasonable to assume that the absorbates which have such an action exist as compounds of the

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[1] T. Imanaka and K. Hirota, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **84**, 193 (1963).
[2] K. Hirota and T. Imanaka, ibid., **84**, 960 (1963).
[3] T. Imanaka and K. Hirota, ibib., **85**, 359 (1964).
[4] T. Imanaka and K. Kishimoto, ibid., **85**, 819 (1964).
[5] H. H. Perkampus and E. Baumgarten, *Ber. der Bunsenges.*, **67**, 576 (1963).

π-electron system, and that the interaction between aluminum chloride and π-electrons promotes the crystallization and the dispersion of evaporated aluminum chloride.

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