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The Mechanism of the Polymerization of Propylene by Evaporated Aluminum Chloride

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The polymerization of propylene with a strictly dry aluminum chloride catalyst was studied by means of the kinetic method in the absence of a solvent. The reaction was also studied by means of infrared (IR) and electronic analysis of the reaction mixture, which had previously been subjected to vacuum evaporation. Besides, the species responsible for the initiating reaction was investigated by a high-resolution mass spectrometer (MS).

The results may be summarized as follows: (1) The presence of a co-catalyst, such as water, hydrogen chloride, or methyl chloride, is indispensable for the reaction, and there is an optimum amount of the cocatalyst. (2) The IR spectrum analysis does not show the formation of a species with an aluminum–carbon bond during the course of the polymerization. (3) A carbonium cation was detected by electronic spectrum analysis. A complex which was produced by the addition of a proton to an aromatic compound was also found. (4) The rate-determining step of the polymerization reaction was examined by using deuterium chloride as a co-catalyst instead of hydrogen chloride, and also by adding compounds with a high dielectric constant during the course of the polymerization. Here an isotopic effect was observed in the apparent activation energy. As the dielectric constant of additives increases, the activation energy decreases and the over-all rate increases. (5) By means of mass spectrometry, species of the H_2AlCl_4 type and the HAl_2Cl_7 type were assumed to exist in the vapor phase of the aluminum chloride–several additives systems.

Finally, it has been concluded that (i) the polymerization of propylene on evaporated aluminum chloride has a cationic mechanism, in which the initiator is an HAl_2Cl_7-type species rather than an $HAlCl_4$-type; that (ii) the initiation takes place over a wide range of time and the step changes with the lapse of time to that of charge transfer, and that (iii) ring formation takes place at the end of the polymer cation in the course of polymerization and the complex is stabilized by a counter ion, leading to the termination reaction.

The Mechanism of Ammonia Decomposition over Iron Synthetic Ammonia Catalysts

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The rate of ammonia decomposition over doubly promoted iron catalysts [(A) containing Al_2O_3 4.72%, K_2O 0.31%, and SiO_2 0.05%; (B) containing Al_2O_3 2.03%, K_2O 0.81%, and SiO_2 0.16%, and (C) containing Al_2O_3 4.72%, K_2O 0.24%, and SiO_2 0.05% as promoters] was followed in a flow system by a differential reactor. The rate, V_+, was found to depend on the partial pressures, P_{NH_3} and P_{H_2}, of ammonia and hydrogen in this manner:

$V_+ = k_1(P_{NH_3}/P_{H_2}1.5)\alpha$ at about 425°C over the (A) and (B) catalysts

$V_+ = k_2(P_{NH_3}/P_{H_2}0.5)\beta$ at about 479°C over the (A) catalyst and about 425°C over (C)

where the constants, k_1, k_2, α, and β, depended sensitively on the experimental conditions.

These results suggest that the rate-determining step of ammonia decomposition over the (A) catalyst changes with a rise in the temperature from the desorption of nitrogen adatoms, $2N(a) \rightarrow N_2$, to the dehydrogenation of the adsorbed amino group, $NH_2(a) \rightarrow NH(a) + H(a)$. The results over (C) indicated that the latter step is rate-determining even at about 425°C if the content of alkali, K_2O, as a promoter is decreased.