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Received January 18, 1971

The Catalytic Activity of α- and β-Aluminum Fluoride

The catalytic properties of aluminum fluoride have been studied relatively little up to now, partly as a consequence of negative results of experiments in the period in which the extreme activity of the other aluminum halides found widespread attention and application (*1*).

It was not until 1962 that Kaiser, Moore, and Odioso (*2*) described the isomerization of pentenes and hexenes, using aluminum fluoride catalysts prepared by prolonged treatment of alumina with concentrated HF solutions. In Russia, Chernov and Antipina (*3*) studied the cracking of isopropyl benzene with a BF_3-activated alumina catalyst; in later experiments (*4*), they also investigated the activity of aluminum fluoride catalysts prepared according to different methods, and found a relation between the activity of these catalysts and their acidity.

The first indications of the existence of two modifications of aluminum fluoride are already relatively old. Thilo (*5*) described, in 1938, the formation of AlF_3 by thermal decomposition of NH_4AlF_4 at 500°C, which compound was formed by heating of $(NH_4)_3AlF_6$ at temperatures below 350°C. Biltz and Rahlfs (*6*) had reported already in 1927 without comment the remarkably low density of AlF_3 obtained in this way, from which it is clear now that it concerned the low density hexagonal β-modification. It was not before 1962, however, that Christoph, Elkton, and Teufer (*7*) clearly distinguished between rhombic α- and hexagonal β-aluminum fluoride by means of X-ray diffraction measurements; the authors claimed the use of the β modification (prepared by dehydration of α-aluminum fluoride trihydrate at relatively low temperatures) as an active and highly selective catalyst for the hydrofluorination of acetylene.

In a recent patent application (*8*), an industrial process for the manufacture of pure anhydrous β-AlF_3 from ammonium fluoride, a by-product of the manufacture of phosphoric acid from fluorine containing phosphate ores, is described (compare Fig. 1).

In the first reaction step an aqueous so-

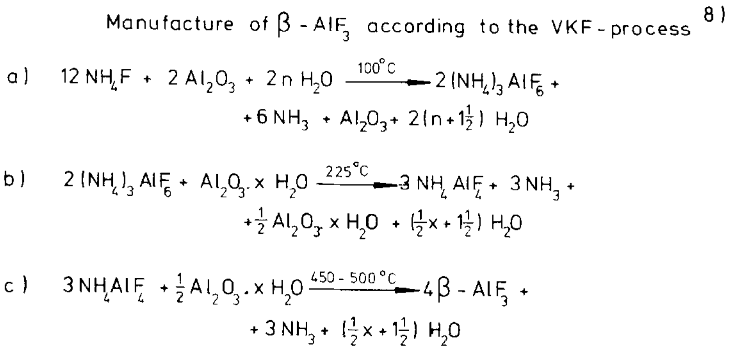

FIG. 1. Manufacture of β-AlF_3 according to the VKF process (*8*).

lution of NH_4F is treated with a 100% excess of activated alumina, prepared, e.g., from gibbsite ($Al_2O_3 \cdot 3H_2O$) by partial dehydration at 300°C. Triammonium hexafluoroaluminate crystallizes out in the pores of the alumina. When the reaction conditions are properly chosen an intimate mixture of $(NH_4)_3AlF_6$ and Al_2O_3 is formed which is transformed completely into β-AlF_3 in the following calcination steps, which can be carried out in a rotating kiln.

An important feature of the VKF process is the possibility of preparing intimate mixtures of β-aluminum fluoride and alumina of any composition, by simply regulating the excess of alumina used in the first reaction step in such a way that the desired end product is obtained. Mixtures of β-AlF_3 and aluminum oxide have been claimed as highly active catalysts for the disproportionation of toluene (*9*). As was demonstrated by Shinn (*10*) the metastable β-AlF_3 is transformed irreversibly into the stable α-modification by prolonged heating at temperatures of approximately 720°C.

EXPERIMENTAL

Cracking Experiments of n-Hexane with α- and β-AlF_3

Cracking experiments with *n*-hexane (olefin-free), using α- and β-AlF_3 as catalysts, were carried out in a micropulse reactor in conjunction with a gas chromatograph at temperatures varying from 300–560°C, and at atmospheric pressure. The amount of catalyst was approximately 2 g in each experiment. The catalysts were activated by heating them in a helium flow (approx. 60 ml/min) at approximately 500°C during the night. After the desired reaction temperature was established, a

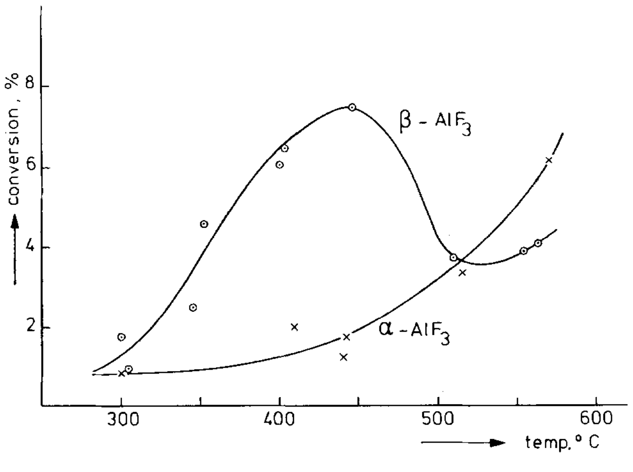

FIG. 2. Conversion of *n*-hexane with α- and β-AlF_3 at different temperatures.

pulse (approx 1 μliter) of n-hexane was introduced at the top of the reactor; the reaction products were collected in a cold trap and, after the actual experiment, transported to the gas chromatograph by replacing the liquid nitrogen around the trap by a hot oil bath (115°C). The results of a number of experiments are represented in Fig. 2.

Remarkable is the rather abrupt decrease in activity of β-AlF_3 at temperatures above 450°C, in all probability due at least in part to transformation of the catalyst into the inactive α modification. The results of the product analysis showed a pronounced preference of β-AlF_3 over α-AlF_3, to form butenes and pentenes, particularly in the temperature range of optimal activity; this preference disappears at higher temperatures when also the activity of the catalyst diminishes.

Cracking Experiments of Isopropyl Benzene with α- and β-AlF₃/Alumina Catalysts

Cracking experiments with cumene were executed in a pulse reactor with a number of catalysts consisting of alumina and distinct amounts of α- or β-AlF_3.

The β-AlF_3/alumina catalysts were prepared according to the general outlines of the VKF process (*8*), using such an excess of alumina (prepared by dehydration of gibbsite at 300°C) in the primary reaction step that in the end products the desired ratios of β-AlF_3 and Al_2O_3 were present. Six catalysts were available, containing 10, 20, 40, 60, 80, and 100% β-AlF_3, respectively. To prepare the corresponding mixtures of Al_2O_3 and α-AlF_3, a part of each of the catalysts was submitted to prolonged heating at 550°C, until the X-ray diffraction pattern showed that the conversion of β- into α-AlF_3 was complete.

In the experiments the catalysts were activated by heating them at 450°C in a dry air flow during the night; after replacement of the air flow by helium, seven pulses of cumene were introduced into the helium flow at successively decreasing temperatures of 450, 400, 350, and 300°C, and again at increasing temperatures of 350, 400, and 450°C, each pulse not before stationary experimental conditions as to temperature, pressure, and flow of carrier gas had been obtained. Benzene and propylene appeared to be the only reaction products. The results of a number of experiments are represented in Fig. 3a and b, which hold for the mixtures of alumina with α- and β-aluminum fluoride, respectively. They show the remarkable differences in activity of the α- and the β-AlF_3 compositions at several temperatures. The main conclusions that can be drawn from these preliminary experiments concern their good reproducibility and the optimal activity of mixtures of alumina with 30–70% β-AlF_3, these compositions resulting in 100% conversion at

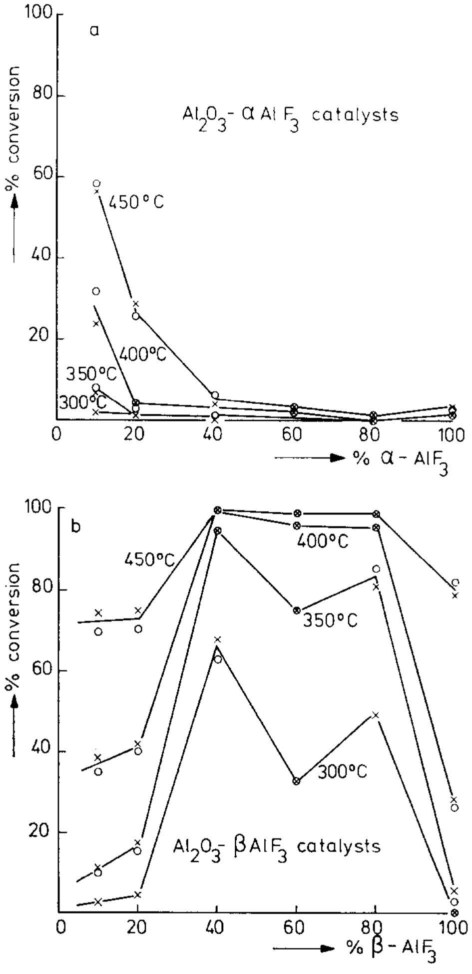

FIG. 3. Cracking experiments of isopropyl benzene with several Al_2O_3/α-AlF_3 and Al_2O_3/β-AlF_3 catalysts at different temperatures.

400°C. The compositions with the α-modification all show a very poor activity.

No relation could be found between catalytic activity, the specific surface, and the number of acid sites of the catalysts. The specific surface of the α- and β-AlF_3 samples is rather low, and amounts to 10–30 m^2/g; the specific surface of the activated gibbsite used for the preparation of the mixed catalysts amounts to approximately 300 m^2/g; values for the catalysts are between these extremes. The acidity of the alumina–β-AlF_3 catalysts was determined according to the method described by Moscou and Lakeman (*11*), using $LiAlH_4$ as the reactant; values for the number of acid sites per gram of catalyst show a more or less regular decrease with increasing AlF_3–Al_2O_3 ratios (compare Fig. 4), but no relation with the cracking activity of the catalysts.

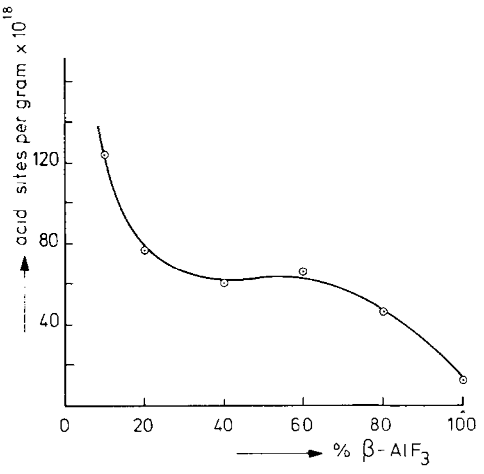

FIG. 4. Acidity of mixed Al_2O_3–β-AlF_3 catalysts.

ACKNOWLEDGMENTS

The authors' thanks are due to Mr. E. B. Vriezen for his contribution in the acidity measurements. The catalysts were prepared by Mr. Th. J. Thoonen, and put kindly at our disposal by the Development Dept. of the Verenigde Kunstmest Fabrieken Mekog-Albatros N.V. at Utrecht.

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