Studies on BF₃-Complex Catalysts in the Alkylation Reaction of Benzene Homologues

Part I. The Deterioration of BF₃-H₂O Catalyst in Alkylation Reactions at Room Temperature

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Summary: The catalytic behaviors of the BF₃-H₂O catalyst in the alkylation of benzene with propylene were observed and discussed with special reference to the deterioration of the catalyst during the course of the reaction at room temperature. The activity of the BF₃-H₂O complex was very high and almost constant for some time in the early stage of the reaction, and then decreased very suddenly. The main cause of this deterioration of the catalyst was neither the desertion of BF₃ from the catalyst nor the accumulation of propylene polymers on the catalyst but the chemisorption of feed propylene to the catalyst.

By hydrolysis of the spent catalyst, isopropyl ether (II) and isopropyl alcohol (III) were obtained. This result suggested the existence of the ester type intermediate (I) presumably formed by a combination of the chemisorbed propylene with the catalyst.

\[
\text{CH}_3\text{CH=CH}_2 + \text{H}^+\text{BF}_3\text{OH}^- \rightarrow \left(\begin{array}{c}
\text{CH}_3 \\
\text{CH}_2 \\
\end{array}\right) \cdot \left(\begin{array}{c}
\text{CH}_3 \\
\text{CH} \\
\end{array}\right) \cdot \text{BF}_3\text{OH}^-
\]

And the following equilibrium relations might be considered.

\[
\begin{align*}
\text{CH}_3\text{CH=CH}_2 + \text{H}_2\text{O} & \rightarrow \text{CH}_3\text{CHCH}_3 + \text{CH}_3\text{CH}_2\text{OH} \\
\text{CH}_3\text{CH=CH}_2 + \text{H}_2\text{O} & \rightarrow \text{CH}_3\text{CHCH}_2\text{OH} + \text{H}^+\text{BF}_3\text{OH}^-
\end{align*}
\]

The possibility of regeneration of the spent catalyst through long standing or heating may be suggested by the above mentioned relations.

Introduction

Boron trifluoride is one of the recently developed catalysts in the field of petroleum chemistry. It is generally used in the form of complexes with organic and inorganic substances containing a lone pair of electrons\(^1\),\(^2\).

In this paper, the catalytic behaviors of the BF₃-H₂O catalyst in the alkylation of benzene with propylene were observed and discussed with special reference to the deterioration of the catalyst during the course of the reaction.

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catalyst to cause its deterioration.

The aim of this study is to find out the positive causes for the catalyst deterioration.

Apparatus and Experimental Procedure

The alkylation was conducted in a 4-necked flask containing the catalyst and benzene (chemically pure) fitted with a mechanical stirrer, a thermometer and a reflux condenser, as shown in Fig. 1, under normal pressure and in the temperature range of 20-70° C.

Propylene was introduced into the reaction flask at a constant flow rate. The reaction took place in a heterogeneous liquid phase system. After the reaction, the alkylate layer and the catalyst layer were separated from each other and the products were analysed by gas chromatography and infrared spectroscopy.

Boron trifluoride monohydrate (BF₃·H₂O) was used as the catalyst for each experiment. It was easily produced by introducing BF₃ gas into H₂O.

To determine the concentration of BF₃ in the BF₃·H₂O complex thus produced, the alkali titration method⁵⁻⁷, using methyl orange as an indicator, in the presence of CaCl₂, was successfully used. The neutralization proceeded according to the following equations:

\[
2(BF₃·H₂O) + 3CaCl₂ + 4H₂O \xrightarrow{\text{heat}} 3CaF₂ + 6HCl + 2H₃BO₃
\]

\[
\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + H₂O
\]

\[
\text{BF}_₃/\text{H}_₂\text{O} \text{ mole ratio} = \frac{(B/M.\text{W. of BF}_₃)/((A-B)/M.\text{W. of H}_₂\text{O})}{\text{Weight of BF}_₃ \text{ in A g of BF}_₃·\text{H}_₂\text{O complex determined by the titration}}
\]

\[
\text{Weight of BF}_₃ \text{ in A g of BF}_₃·\text{H}_₂\text{O complex determined by the titration}
\]

\[
\text{Weight of water in A g of BF}_₃·\text{H}_₂\text{O complex (A-B) g}
\]

Propylene is contained in the sample (A g) of the spent catalyst. However, in most cases, the amount of the absorbed propylene in the spent catalyst is a negligible quantity. Hence, BF₃ concentration in the spent catalyst is almost the same as the BF₃/\text{H}_₂\text{O mole ratio}.

Experimental Data and Discussion of the Results

The effect of the reaction temperature on the life of the BF₃·H₂O complex catalyst

The effect of the reaction temperature on
the catalyst life was observed in the range of 20° to 70°C. The results are shown in Fig. 2.

According to our experimental results⁸, the active form of BF₃·H₂O complex is a proton donor substance (H⁺BF₃OH⁻) formed by the combination of free BF₃ and solvated BF₃ (H₃OBF₃OH⁻) in the BF₃·H₂O system.

\[ H₃OBF₃OH⁻ + BF₃ → 2H⁺BF₃OH⁻ \]

Hence, the existence of free BF₃ in the system is absolutely necessary for the appearance of the active complex form.

From this standpoint, since BF₃ in the BF₃·H₂O system is comparatively stable at lower temperatures, it may be said that low temperature favors the elongation of the catalyst life.

However, as shown in Fig. 2, the life of the catalyst was extremely short at the reaction temperature of 20°C and maximum at 50°C. At 70°C and higher temperatures the catalyst showed to decrease its life.

The saturated aqueous solution of BF₃ had the composition of BF₃/H₂O=0.94~0.96 (mole ratio) at room temperature. When this solution was heated at 70°C for a while, it evolved BF₃ to give the BF₃/H₂O ratio of below 0.7, losing its catalytic activity at the same time.

The effect of the BF₃ concentration in BF₃·H₂O complex on the catalytic activity

The alkylation of benzene with propylene was carried out with the catalysts having the same amount of BF₃ in different mole ratio of BF₃/H₂O. The activity of each catalyst was given by the absorption amount of propylene. The results are shown in Fig. 3.

The catalysts showed high activity when the BF₃/H₂O ratio was higher than 0.8 (mole ratio). The activity decreased gradually.
corresponding to the decrease of the concentration of BF$_3$ in the catalyst. In the range where the BF$_3$/H$_2$O ratio of the catalyst complex was 0.5 and lower, the catalyst was quite inactive.

Properties of the spent catalyst

Propylene was conducted into a reaction vessel containing 1 mole of benzene and 8 g of BF$_3$-H$_2$O complex (BF$_3$/H$_2$O mole ratio = 0.95) at a rate of 0.3 l/min at 20°C until no more propylene absorption was observed.

After the reaction was discontinued, the spent catalyst, a milky colored liquid, was separated carefully from the alkylated products and was allowed to stand at room temperature. After a while, the homogeneous spent catalyst separated into two layers with violent heat evolution. The flow sheet of the treatment of the spent catalyst is shown in Fig. 4.

Judging from the gaschromatogram and the results of the infrared spectroscopic determination of the narrow cuts of the upper layer oil obtained by the gaschromatographic separation (See Fig. 5), the upper layer consisted of polypropylbenzenes and propylene polymers mainly produced by the secondary reactions of propylene adsorbed by the catalyst.

When the spent catalyst was settled at 0~5°C, an oil layer separated out. The oil had the same composition as that of the alkylated products. Hence, this oil was considered to be a portion of the alkylated products physically adhered to the catalyst.

After the separation of the oily layer, the spent catalyst was allowed to stand again at room temperature. By this treatment, another oil layer separated out. The gaschromatogram of this oil (See Fig. 6) showed it consisted mainly of propylene polymers. The propylene polymers were also identified by infrared spectroscopic determination of the oil fractions. Hence, polymerization of the adsorbed propylene seemed to take place while the spent catalyst stood at room temperature.

On the other hand, when water was added to the spent catalyst, an oil layer (B) was also obtained. The gaschromatogram of this oil layer is shown in Fig. 7.

Isopropyl ether, isopropylalcohol and aromatic hydrocarbons having the same compo-
sition as that of the alkylate products were identified. The ether and the alcohol were also found in the lower aqueous layer.

The spent catalyst, carefully separated from the physically adhered alkylated products by settling at 0~5°C, also gave a considerable amount of ether and alcohol by dilution with water.

**Change in the BF₃ concentration of the catalyst in the course of reaction**

A decrease in the BF₃ concentration of the catalyst due to the liberation of unstable BF₃ in the BF₃–H₂O system was observed in the early stage of each experiment.

The BF₃ concentration of the catalyst was analysed after each run (each run having a different duration of time).

The spent catalyst was allowed to settle for three days before the analysis to separate the adhered propylene from the catalyst. The results are shown in Fig. 8.

As shown in Fig. 8, the decrease in the BF₃ concentration was remarkable in the warming-up stage prior to the reaction. When the reaction proceeded, the BF₃ concentration decreased very gradually for a certain duration.

Hence, the initial decrease in the BF₃ concentration due to BF₃ gas liberation did not seem to be responsible for the catalyst deterioration during the reaction.

In Fig. 9, percent of absorbed propylene to conducted propylene is plotted against the amount of conducted propylene at the reaction temperature of 20°C. The BF₃ concentration of the catalyst was determined after settling for 24 hrs to remove the adhered propylene.

As shown in Fig. 9, the catalyst lost its activity when the BF₃/H₂O mole ratio fell to 0.84 from the initial value of about 0.96.

However, the value of 0.84 was obtained after standing the catalyst for 24 hrs. This value should be lower, if the concentration measuring were conducted just after the reaction was stopped.

The change in the BF₃/H₂O mole ratio of the spent catalyst during standing was caused by the separation of the adsorbed propylene from the catalyst. (See previous section. "Properties of the spent catalyst" in this paper.)

As a result, it may be said that the main cause of the catalyst deterioration is not the desertion of free BF₃ from...
the catalyst complex, but the adsorption of propylene to the catalyst.

In order to confirm the chemisorption of propylene to the catalyst, the following experiments were carried out.

Propylene was introduced into the mixture of 1 mole of benzene and 8.0 g of BF₃-H₂O complex (BF₃/H₂O=0.95) at a rate of 0.31/min at 20°C. The reaction was discontinued after a certain duration. The catalyst layer was carefully separated from the reaction product and settled for 24 hrs at 0~5°C.

After removing the separated oil 7.5 g of the catalyst was dissolved in 100 ml of water. This aqueous solution was examined by means of gas chromatograph equipped with a flame ion detector.

As shown in Fig. 10, *the adsorbed propylene was converted into isopropyl alcohol and isopropyl ether by hydrolysis. And the amount of these propylene derivatives increased corresponding to the increase in the amount of conducted propylene.

The spent catalysts regained their BF₃/H₂O mole ratio value nearly up to the initial value of 0.95 by long standing at room temperature with the separation of oily substances.

The lower the reaction temperature, the faster the spent catalyst regained its BF₃ concentration as shown in Fig. 11. And the spent catalyst of the reaction at 20°C regained its initial BF₃ concentration almost completely after standing four days. While in the case of the catalysts of the reactions at 50°C and 70°C, the recovery of the BF₃ concentration required over one month's standing and yet complete recovery could not be achieved. It is believed that this result was due to the liberation of BF₃ during the reaction at high temperatures.

It was reported that olefin polymers deteriorated the BF₃-catalyst and these results were also confirmed by us (See Fig. 12). However, in the circumstances under which our alkylation experiments were conducted, propylene polymers were not found to any appreciable extent.

The Relationship between the flow rate of propylene and the catalyst life

The effect of propylene feed rate on the life of catalyst was observed at the reaction temperature of 20°C. The results are shown in Fig. 13.

In the case of using the same amount of the catalyst for each run, it was observed that the lower the feed rate of propylene, the longer the life of the catalyst.
catalyst and the greater the amount of propylene reacted in total.

On the other hand, the effect of the amount of the catalyst on the catalyst life was also observed at a constant flow rate of propylene. The results are shown in Fig. 14.

It was observed that the total amount of the reacted propylene increased very rapidly with the increase in the catalyst amount. A roughly linear relation seemed to hold between the catalyst amount and logarithm of the amount of reacted propylene. However, further discussion will be necessary on this problem.

Regeneration of the spent catalyst

When the BF3-H2O complex lost the catalytic activity in the propylation of benzene at the reaction temperature of 20°C, the reaction system was allowed to stand for 24 hrs at room temperature. After this treatment, the propylation reaction was continued again.

As apparently observed in Fig. 15, the activity of the catalyst was almost recovered. Hence, under these circumstances, it was necessary to settle the reaction mixture for 24 hrs or more in order to recover the catalyst activity.

The catalyst recovered its activity very rapidly when the reaction mixture was heated at 50°C, instead of standing at room temperature. The results are shown in Fig. 16.

Conclusions

As mentioned above, it may be concluded that the main cause of the deterioration of the BF3-H2O complex catalyst in the propy-
lation of benzene at the reaction temperature of 20°C was neither the desertion of BF$_3$ from the catalyst nor the accumulation of propylene polymers on the catalyst but the chemisorption of feed propylene to the catalyst. In this case, the chemisorption of propylene to the catalyst took place more easily at lower alkylation temperatures. Hence, the lower was the alkylation temperature, the faster the catalyst deteriorated.

This consideration agreed exactly with the experimental results showing the reaction temperature affect on the life of the catalyst.

The mechanism of the chemisorption of propylene to the BF$_3$-H$_2$O complex catalyst was considered as following from the results of the spent acid hydrolysis.

\[
\text{BF}_3\cdot\text{H}_2\text{O} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5^+ + \text{BF}_3\text{OH}^- + 3\text{H}_2\text{O}
\]

BF$_3$-H$_2$O complex is a well-known protonated acid which converts propylene into propyl carbonium ion in the propylation of benzene. At the same time, by combining with propylene, it forms an ester type intermediate having no catalytic activity. However, considering both the ester formation and the carbonium ion formation as equilibrium reactions, the following relations may be proposed:

\[
\text{CH}_3\cdot\text{CH} = \text{CH}^- + \text{H}^+ + \text{BF}_3\text{OH}^- \rightarrow \left(\begin{array}{c}
\text{CH}_3^+ \\
\text{CH}_3\cdot \text{BF}_3\text{OH} \end{array}\right)
\]

\[
\text{CH}_2\cdot\text{CH} - \text{CH}_3 + \text{CH}_4\cdot\text{CH} - \text{CH}_3 + \text{H}^+ + \text{BF}_3\text{OH}^- \rightarrow \text{CH}_3\cdot\text{CH} - \text{CH}_3 + \text{BF}_3\text{OH}^- + \text{OH}
\]

The above relation may suggest the possibility of regeneration of the spent catalyst by long standing or heating.

References