# New approaches to immobilization of aluminum chloride on $\gamma$-alumina and its regeneration after deactivation

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The preparation of an $AlCl_3$ catalyst immobilized on $\gamma$-$Al_2O_3$ and its regeneration after deactivation have been studied. $AlCl_3$, generated by reacting $CCl_4$ with $\gamma$-$Al_2O_3$, was carried by $N_2$ to a reactor containing the $\gamma$-$Al_2O_3$ support. The immobilized $AlCl_3$ catalyst with meso- and macro-pore bimodal structure was shown to be suitable for isobutene oligomerization. The amount of $AlCl_3$ immobilized on the support in terms of $AlCl_x$ ($x = 2.2$) was 7.5 wt%. The catalyst exhibited excellent catalytic properties for isobutene polymerization under mild conditions. The average molecular weight of the product was 1000–2500, and its distribution was narrow, around 2.0 in the reaction temperature range 10–40 °C. This catalyst showed nearly perfect reactive specificity to isobutene polymerization and remarkable stability. After 2000 h of continuous running, the conversion dropped from 99 to 57%, the selectivity was maintained with little change at about 90%, and the average molecular weight was within the range 1000–1200 under the conditions $T = 32 \pm 1\,°C$, $LHSV = 2.0\,h^{-1}$, and $P = 1.0\,MPa$.

Regeneration of the deactivated catalyst was satisfactorily accomplished by treating the used catalyst with a saturated solution of $AlCl_3$ in $CCl_4$ either *in situ* or *ex situ*. The activity recovery can be as high as 96%, and the deactivated catalyst can be regenerated repeatedly.

**KEY WORDS:** aluminum chloride; $\gamma$-alumina; immobilization; regeneration; isobutene polymerization.

## 1. Introduction

$AlCl_3$ is one of the important Friedel–Crafts catalysts widely used in the chemical, petroleum refining, and pharmaceutical industries. It manifests excellent catalytic properties in alkylation, acylation, alkene isomerization, cracking, and polymerization processes. Unfortunately, its applicability is seriously hindered on account of its drawbacks, such as corrosiveness, difficulty of separating the used catalyst from products, and production of a large amount of environment-polluting wastes. A promising improvement of traditional $AlCl_3$ catalysts is the immobilization of $AlCl_3$ on a support. The immobilization of $AlCl_3$ catalysts was first successfully applied in World War II in the isomerization of *n*-butane to produce isobutene and other fuel oils [1].

Immobilization of $AlCl_3$ on supports such as $Al_2O_3$, $SiO_2$, etc., was mainly achieved through the reaction of $AlCl_3$ with the support in the gas–solid phase [2] or in the gas–solid phase using $CCl_4$ or $CHCl_3$ as the solvent for $AlCl_3$ [3]. The most studied method of preparing immobilized $AlCl_3$ catalyst is the chlorination of $Al_2O_3$ by chlorine-containing compounds such as $CCl_4$, $CHCl_3$, $CH_2Cl_2$, etc., in the polymerization of 4-methyl-1-pentene [4], the copolymerization of propylene and butanes [5], and the polymerization of isobutene [6–8]. The prepared immobilized catalysts were effectively used in the polymerization of isobutene and other lower olefin monomers. Such catalysts have greatly remedied the drawbacks of traditional $AlCl_3$ catalysts, but there remains room for improvement in catalytic properties. Recently, we reported a chlorinated $Al_2O_3$ catalyst, which was prepared by a one-step reaction of $CCl_4$ with $\gamma$-$Al_2O_3$ [9]. It showed high catalytic activity in isobutene polymerization, but its repeatability and stability were found to be unsatisfactory.

In this work, a novel two-step method of preparing immobilized $AlCl_3$ catalysts having excellent stability and repeatability has been developed. Freshly generated $AlCl_3$ was made to react with $\gamma$-$Al_2O_3$ having meso- and macro-pore bimodal structure. The prepared catalysts showed excellent properties in isobutene polymerization under mild conditions. Regeneration of the deactivated catalyst was accomplished with a high recovery of activity by treating it with a saturated solution of $AlCl_3$ in $CCl_4$ either *in situ* or *ex situ*.

## 2. Experimental

### 2.1. Materials

Three kinds of $\gamma$-$Al_2O_3$ were used as supports, and their physicochemical parameters are listed in table 1. $\gamma$-$Al_2O_3$ supports of A-1 and A-2 were supplied by SINOPEC Changing Petroleum Processing and Chemical Company, A-3 by China Research Institute

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Table 1
Physicochemical parameters of $\gamma$-$Al_2O_3$

| | A-1 | A-2 | A-3 |
|---|---|---|---|
| Specific surface area ($m^3/cm^3$) | 196.45 | 178.68 | 122.29 |
| Packing density ($g/cm^3$) | 0.8 | 0.75 | 0.575 |
| Pore volume ($cm^3/g$) | 0.45 | 0.55 | 1.513 |
| Average pore diameter (Å) | 16.6 | 26.8 | 15840 |

Table 2
Composition of $C_4$ fraction hydrocarbon mixture

| Composition | $C_4^0 + i\text{-}C_4^0$ | t-2-$C_4^=$ | c-2-$C_4^=$ | 1-$C_4^=$ | i-$C_4^=$ |
|---|---|---|---|---|---|
| Content (wt%) | 18.2 | 8.1 | 2.9 | 43.1 | 27.7 |

of Daily Chemical Industry. The $C_4$ hydrocarbon mixture feed was provided by Petro-China, Jilin Chemical Industrial Company. Its composition is given in table 2.

### 2.2. Preparation of the catalyst

Forty-eighty mesh (unless specially noted) $\gamma$-$Al_2O_3$ was calcined at 400 °C under a $N_2$ stream for 2 h, and then the temperature was lowered to 300 °C. $AlCl_3$, which was produced in another reactor by reacting $CCl_4$ with pure $\gamma$-$Al_2O_3$ of high purity at 500 °C, was carried to the reactor containing the pretreated $\gamma$-$Al_2O_3$ by a $N_2$ stream. The reaction between $AlCl_3$ and $\gamma$-$Al_2O_3$ was allowed to proceed for 4 h at 300 °C unless specially noted, and the adsorbed $AlCl_3$ was removed by flushing with $N_2$ at 400 °C for 1 h. The catalyst was then cooled to room temperature under a $N_2$ stream. Catalysts on supports A-1, A-2, and A-3 were denoted by AC-1, AC-2, and AC-3, respectively. The analytical results indicated that the mole ratio Cl/Al of the active species on the surface of the immobilized catalyst was 2.2 (table 3).

### 2.3. Apparatus and procedures

The polymerization of isobutene was carried out in a fixed-bed reactor, working under the conditions of $\text{LHSV} = 2.0\,\text{h}^{-1}$ and pressure = 1.0 MPa. This pressure is sufficient to keep the $C_4$ hydrocarbon mixture in the liquid state at the reaction temperature. The reactor was a stainless steel tube (ID = 16 mm, $h = 550$ mm) with a water jacket that allowed the reaction temperature to be maintained to within ±0.5 K by circulating water in a thermostat bath. A liquid $C_4$ mixture containing isobutene was fed into the reactor from below by a syringe pump. After depressurization by a back-valve to atmospheric pressure, the unreacted gas was passed through a gas–liquid separator, and measured by a rotameter. A steady state was reached after about 4–6 h.

### 2.4. Analytical methods

The composition of the feed and the effluent gas were analyzed using a GC, FID, with a 4 mm × 3 m packing column of silver nitrate–ethylene glycol on 6210 red carrier. $W_1$ represents the weight of the crude product, which was obtained by treating the primary product under a pressure of 200 torr and ambient temperature for 30 min, to remove the dissolved $C_4$ component. The crude product, of weight $W_1$, was further treated under 60 torr and at 125 °C for 1 h to remove isobutene dimer and some trimer. $W_2$ is the weight of the final product. The selectivity of the product is defined as:

$$\text{selectivity} = \frac{W_2}{W_1} \times 100\%.$$

The conversion of isobutene was calculated from its concentrations in both the feed and the effluent gas determined using GC with *n*- (iso-) butane as the internal standard. The average molecular weight ($\overline{M_n}$) and its distribution ($D$) were determined using a GPC (JASCO Company). The chlorine content of the catalysts was determined by the Vol hard method [10].

## 3. Results and discussion

### 3.1. Effect of reaction conditions of immobilization of $AlCl_3$ on the catalytic properties

The effect of the reaction conditions of immobilization of $AlCl_3$ on the catalytic behavior of the

Table 3
Effect of temperature of $AlCl_3$ immobilization on the composition and catalytic properties of the catalyst [a]

| Temp. (°C) | Percentage of $AlCl_x$ (wt%) | Cl/Al (mol%) | Catalytic behavior: polymerization of isobutene [b] | | |
|---|---|---|---|---|---|
| | | | Conversion (%) | Selectivity (%) | Average mol. wt ($\overline{M_n}$) |
| 250 | 7.5 | 2.2 | 93.8 | 83.2 | 1160 |
| 300 | 7.5 | 2.2 | 94.1 | 92.2 | 1311 |
| 350 | 7.3 | 2.2 | 95.5 | 91.1 | 1342 |
| 400 | 7.2 | 2.2 | 94.2 | 92.3 | 1390 |

[a] Immobilization conditions: $V_{\gamma\text{-}Al_2O_3} = 15\,\text{ml}$, $F_{CCl_4} = 2.01\,\text{ml/h}$, $t = 4\,\text{h}$.
[b] Reaction conditions: $T = 30\,°\text{C}$, $P = 1.0\,\text{MPa}$, $\text{LHSV} = 2.0\,\text{h}^{-1}$.

Table 4
Effect of duration of $AlCl_3$ immobilization reaction on catalytic properties[a]

| Time (h) | Percentage of $AlCl_x$ (wt%) | Cl/Al (molar ratio) | Catalytic property in isobutene polymerization[b] | | |
|---|---|---|---|---|---|
| | | | Conversion (%) | Selectivity (%) | Average mol. wt of product ($\overline{M_n}$) |
| 0.5 | 7.5 | 2.2 | 94.8 | 89.0 | 1282 |
| 1.0 | 7.5 | 2.2 | 94.6 | 91.3 | 1320 |
| 2.0 | 7.4 | 2.2 | 93.5 | 89.9 | 1245 |
| 3.0 | 7.4 | 2.2 | 94.6 | 91.1 | 1306 |
| 4.0 | 7.5 | 2.2 | 94.1 | 92.2 | 1311 |

[a] Immobilization conditions: $V_{\gamma\text{-}Al_2O_3} = 15\,ml$, $F_{CCl_4} = 2.01\,ml/h$, $T = 300\,°C$.
[b] Reaction conditions: $T = 30\,°C$, $P = 1.0\,MPa$, $LHSV = 2.0\,h^{-1}$.

immobilized catalyst is shows in table 3. From this table, it can be seen that conversion, selectivity, and average molecular weight are somewhat lower when the reaction temperature is 250 °C. Within the temperature range 300–400 °C, conversion and selectivity of the catalyst practically remain constant. When the reaction temperature increases, the average molecular weight shows a tendency to increase slightly.

The results of the effect of reaction time of immobilization on the amount of $AlCl_x$ (wt%), Cl/Al mole ratio, and the behavior of the obtained catalyst are given in table 4.

At 300 °C, and within the time range of immobilization of 0.5–4.0 h, the catalysts obtained show little difference in the content of $AlCl_x$, Cl/Al mole ratio, and catalytic behavior. This indicates that the reaction between $AlCl_3$ and hydroxyl groups on the surface of $\gamma$-$Al_2O_3$ takes place very fast. It might be accomplished in a period of much less than half an hour.

Table 5 gives the effect of feeding rate of $CCl_4$ on catalytic properties. In preparing the immobilized catalyst, a supply of $AlCl_3$ at a rate of 11.2–27.8 mmol/h to 15 ml $Al_2O_3$ seems to be sufficient, since the obtained catalysts within this range of flow of $AlCl_3$ exhibit almost identical catalytic properties.

### 3.2. *Influence of the pore structure of the catalyst on the catalytic behavior*

It was found that the pore structure of the catalyst plays a very important role in the catalytic behavior in the oligomerization of isobutene. From figure 1, it can be seen that the three catalysts have high activity, but they differ widely in the decrease of activity in the course of reaction. AC-1 with micro-pores of average diameter 15.6 Å shows the steepest fall in activity; its conversion falls from 98 to 70% in 150 h. The initial conversion over AC-2 with meso-pores of average diameter 26.8 Å, which is nearly identical with that of AC-1, falls to 81% after 200 h of running. AC-3 displays the slowest decrease of conversion and can still maintain 94% isobutene conversion after 500 h continuous running. According to the results of a pore distribution study, in the AC-3 catalyst there are 30% of pores with diameter 120–400 Å, 43.3% with diameter of 12 000–28 000 Å, and 8.6% with diameter larger than 28 000 Å. The decrease of conversion over the catalysts having micro- and meso-pore structures can be ascribed to pore clogging of the catalyst resulting from the stagnation and accumulation of slowly diffusing large polyisobutene molecules within the pores of the

Table 5
Effect of feeding rate of $CCl_4$ on catalytic properties[a]

| Feeding rate of $CCl_4$ (ml/h) | Flow of $AlCl_3$ (mmol/h) | Catalytic property in isobutene polymerization[b] | | |
|---|---|---|---|---|
| | | Conversion (%) | Selectivity (%) | Average mol. wt of product ($\overline{M_n}$) |
| 0.80 | 11.1 | 92.7 | 85.6 | 1129 |
| 1.15 | 15.9 | 94.2 | 91.7 | 1270 |
| 1.50 | 20.7 | 95.9 | 91.6 | 1285 |
| 2.01 | 27.8 | 94.1 | 92.2 | 1311 |

[a] Immobilization conditions: $N_2 = 40\,ml/min$, $t = 4\,h$, $V_{\gamma\text{-}Al_2O_3} = 15\,ml$.
[b] Reaction conditions: $T = 30\,°C$, $P = 1.0\,MPa$, $LHSV = 2.0\,h^{-1}$.

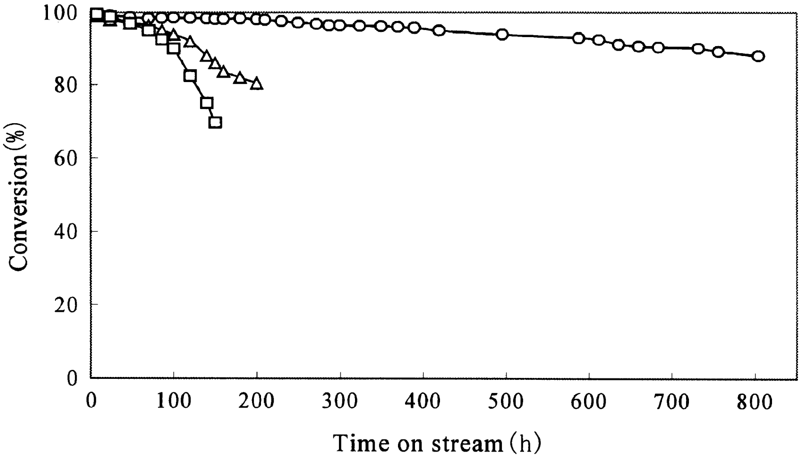

Figure 1. Effect of pore structure of support on the activity of the catalysts. Reaction conditions: $T = 32 \pm 1\,^{\circ}\mathrm{C}$, $\mathrm{LHSV} = 2\,\mathrm{h}^{-1}$, $P = 1.0\,\mathrm{MPa}$. □, A-1; △, A-2; ○, A-3.

catalyst. Therefore, AC-3 with bimodal meso- and macro-pore structure is preferable for the polymerization of isobutene.

### 3.3. *Catalytic behavior of the immobilized $AlCl_3$ catalyst in isobutene polymerization*

The immobilized $AlCl_3$ on $\gamma$-$Al_2O_3$ having meso- and macro-pore bimodal structure prepared by the improved two-step method shows excellent catalyst behavior. This can be illustrated through discussions about the effects of reaction conditions on the activity of the catalyst, its selectivity, and stability.

#### 3.3.1. *Effect of reaction conditions on the polymerization of isobutene*

It is well known that reaction temperature and control of heat transfer of the reaction system exert great influence on the polymerization of olefins. The results of the study of the effect of temperature within the temperature range 10–40 °C on isobutene polymerization are given in table 6. Isobutene conversion increases with increase in temperature, while selectivity decreases, and the average molecular weight of the product becomes lower and its distribution broader with increasing temperature. A polyisobutene product having $\overline{M_n} \sim 1000$–$1200$ can be obtained at an appropriate reaction temperature of 30–40 °C.

As indicated in table 7, when the space velocity increases, conversion decreases, but, at the same time, selectivity increases. Meanwhile the average molecular weight becomes notably higher and its distribution narrower. The cause of these effects lies in the fact that an increase of space velocity means increasing the amount of substrate flowing through unit volume of catalyst. This clearly shows that space velocity is one of the important factors influencing the average molecular weight of the product and its distribution.

The isobutene concentration in the $C_4$ hydrocarbon mixture has a marked influence on its polymerization. Figure 2 shows that with increasing isobutene concentration in the feed, isobutene conversion gradually increases, and approaches 100% when the isobutene concentration reaches 38%. At lower concentrations of isobutene, product selectivity increases with increasing isobutene concentration, and attains a maximum value when the isobutene concentration reaches about 33%. Further increase of isobutene concentration results in a decrease of the selectivity. This suggests that some of the isobutene molecules form considerable amounts of dimers and trimers on weak acid sites on account of

Table 6
Effect of reaction temperature on the polymerization of isobutene[a]

| Reaction temp. (°C) | Conversion (%) | Selectivity (%) | Average molecular weight ($\overline{M_n}$) | Mol. wt distribution (*D*) |
|---|---|---|---|---|
| 10 | 85.0 | 96.0 | 2467 | 1.88 |
| 20 | 91.1 | 95.1 | 1945 | 1.99 |
| 30 | 94.1 | 92.2 | 1311 | 2.05 |
| 40 | 96.1 | 85.8 | 1022 | 2.25 |

[a] Conditions of catalyst preparation: heat treatment, 400 °C, 2 h; immobilization, 300 °C, 4 h; feeding rate of $CCl_4$, 2.01 mol/h. Conditions of polymerization: $P = 1.0\,\mathrm{MPa}$, $\mathrm{LHSV} = 2.0\,\mathrm{h}^{-1}$.

Table 7
Effect of space velocity of feeding on the polymerization of isobutene[a]

| LHSV ($h^{-1}$) | Condition (%) | Selectivity (%) | Average molecular weight ($\overline{M_n}$) | Mol. wt distribution ($D$) |
|---|---|---|---|---|
| 1.0 | 99.0 | 83.8 | 939 | 2.27 |
| 2.0 | 94.1 | 92.2 | 1311 | 2.05 |
| 3.0 | 83.3 | 96.3 | 1570 | 2.00 |
| 4.0 | 75.9 | 97.1 | 1615 | 1.96 |

[a] Conditions for catalyst preparation are the same as those of table 5. Reaction conditions: $T = 30\,^{\circ}C$, $P = 1.0\,MPa$.

too much isobutene. At a definite temperature, the average molecular weight of the product at first increases, and finally attains a constant value.

### 3.3.2. Reactive specificity to isobutene

The catalytic specificity of the immobilized $AlCl_3$ catalyst was investigated by monitoring the change of the values of ratios $n\text{-}C_4^{=}/C_4^{0}$ and $i\text{-}C_4^{=}/C_4^{0}$ in the effluent gas at different reaction temperatures using butane ($n$-butane + isobutane) as the internal standard. Here $n\text{-}C_4^{=}$ signifies the concentration of normal butenes (but-1-ene + but-2-ene), $i\text{-}C_4^{=}$ that of isobutene, and $C_4^{0}$ that of butanes ($n$-butane + isobutane). The results are plotted in figure 3.

From figure 3 it can be seen that the curve of $n\text{-}C_4^{=}/C_4^{0}$ vs. reaction temperature takes the form of a nearly horizontal line. When the temperature is raised from 10 to 40 °C, $n\text{-}C_4^{=}/C_4^{0}$ only decreases from 2.89 to 2.87. This indicates that normal butenes practically do not participate in the polymerization reaction. However, $i\text{-}C_4^{=}/C_4^{0}$ decreases linearly with increase of reaction temperature. From these results, it is reasonable to assume that immobilized $AlCl_3$ on $\gamma\text{-}Al_2O_3$ exhibits very good specificity to the polymerization of isobutene. The slight decrease of the ratio $n\text{-}C_4^{=}/C_4^{0}$ in the effluent gas can be explained by the higher solubility of $n$-butene in liquid polymer product than that of butanes.

### 3.3.3. Stability of the catalyst

The stability of the catalyst was studied with continuous running for 2000 h under conditions of reaction temperature = 32 ± 1 °C and LHSV = 2.0 $h^{-1}$. The results are shown in figure 4, which reveals that in the early period of reaction, conversion dropped very slowly with time, and kept at a value above 90% after 800 h. At the end of the reaction period of 1000–2000 h, the conversion dropped to 57%. The selectivity was maintained at a high value of about 90% throughout the whole reaction, and average molecular weight was in the range 1000–1200.

Deactivation of the catalyst occurred through prolonged running. One of the reasons is the "pore-clogging" effect caused by the stagnation of large product molecules within the pores of the catalyst. Accumulation of large product molecules in the pores hinders the isobutene molecules from making an approach to the active sites of the catalyst, causing temporary deactivation of the catalyst. It can be calculated from the molecular weight distribution (from GPC analysis) that there is still about 1% of polyisobutene having a molecular weight above 10 000 in the product of $\overline{M_n} \sim 1000$

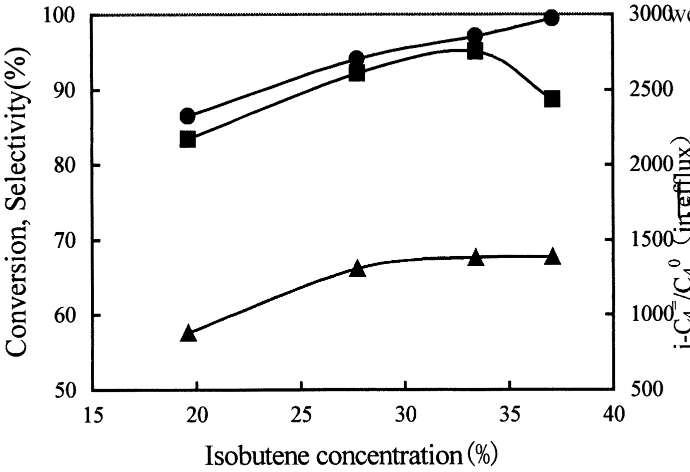

Figure 2. Effect of isobutene concentration on conversion, selectivity, and average molecular weight. Reaction conditions: $T = 30\,^{\circ}C$, LHSV = 2 $h^{-1}$, $P = 1.0\,MPa$. ●, Conversion; ■, selectivity; ▲, average molecular weight.

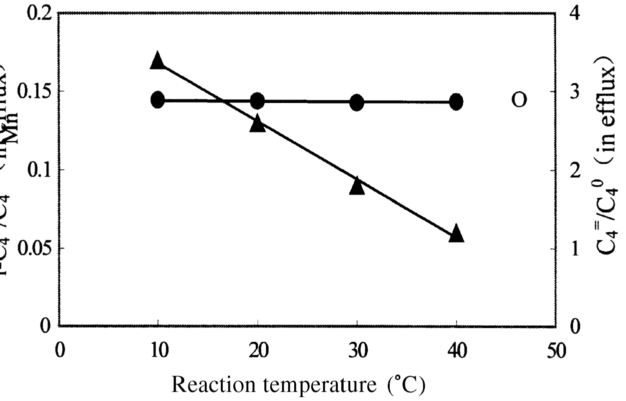

Figure 3. Reaction specificity of the immobilized $AlCl_3$ catalyst to the polymerization of isobutene. Reaction conditions are the same as those of table 3. ▲, Conversion; ●, selectivity; O, $n\text{-}C_4^{=}/C_4^{0}$ (in material).

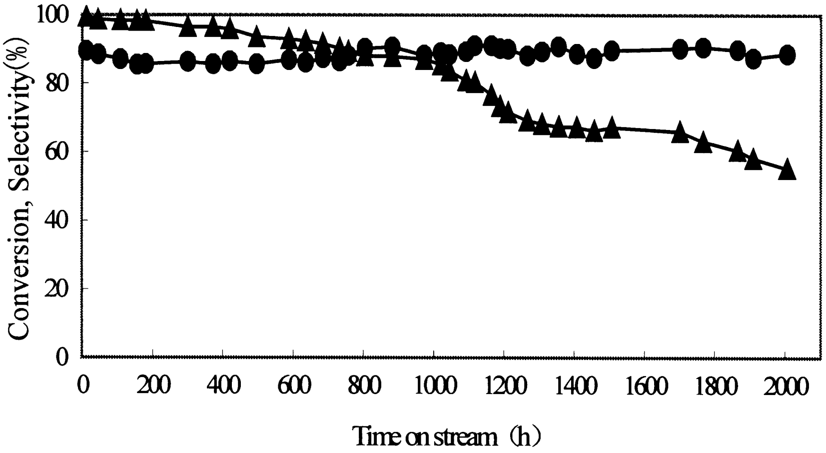

Figure 4. Stability of the catalyst. Conditions of polymerization: $T = 32 \pm 1\,^{\circ}\mathrm{C}$, LHSV = $2\,\mathrm{h}^{-1}$. ▲, Conversion; ●, selectivity.

formed under the above-mentioned reaction conditions. Through the use of supports for immobilization having meso- and macro-pore bimodal structure, such detrimental pore clogging can be greatly reduced, but it cannot be completely eliminated.

Another important reason, possibly the main reason, of deactivation of the catalyst is the poisoning by the residual water in the raw materials. The $C_4$ hydrocarbon mixture, after being dried twice by $\gamma$-$Al_2O_3$, still contains about 10–25 ppm $H_2O$, which can destroy the active component of the catalyst gradually during prolonged running. It is quite possible to further increase the lifespan of the catalyst if the water content in the raw material is further reduced. Other impurities, such as dienes and acetylenes, which are possible to produce polymers, can deactivate the catalyst by covering the active sites with polymeric products. However, since their contents are very low, their influence should be accordingly small.

### *3.4. Regeneration of the deactivated catalyst*

In the case of the deactivation of the catalyst caused by pore clogging the catalyst can be effectively regenerated by interrupting the feed and appropriately raising the temperature to assist the large product molecules to diffuse out of the pores. This kind of deactivation belongs to the category of temporary poisoning. If the deactivation results from trace water poisoning, the catalyst has to be treated chemically to recover the destroyed active complex.

Two methods of regeneration of the deactivated catalyst were suggested, as discussed below.

#### *3.4.1. Regeneration ex situ*

Dry $CCl_4$ (300 ml) and 20 g of freshly prepared $AlCl_3$ were added to a 500 ml three-necked flask equipped with a refluxing condenser and a stirrer. The mixture in the flask was refluxed for 2 h, and then the saturated solution of $AlCl_3$ in $CCl_4$ in the flask was carefully transferred into another three-necked flask of the same size, to which 15 ml of deactivated catalyst were then added under the protection of $N_2$. After being refluxed for 12 h the supernatant $CCl_4$ solution was decanted. The remaining catalyst after being washed with dry $CCl_4$ 1–2 times was flushed with $N_2$ until no $CCl_4$ remained and the catalyst, which assumed a spongy texture, was transferred to the reactor under the protection of $N_2$. Studies on the conversion of the regenerated catalyst were resumed. The results are depicted in figure 5, which reveals that the catalytic properties of the regenerated catalyst have been practically recovered. In the first 950 h of continuous running, the conversion showed a greater decrease than that of the original catalyst. On account of failing to supply feed in time, feeding was interrupted for a period of 50 h. Resumption of feeding after an interruption of 50 h resulted in an increase of conversion of 12% as against that before stopping of feeding. This "automatic reactivation" is probably due to the removal of "pore clogging" to a certain extent. After 1729 h of continuous running, conversion of the auto-reactivated catalyst dropped to 64.9%. However, selectivity and average molecular weight of the product showed no appreciable change.

#### *3.4.2. Regeneration in situ*

The partially deactivated catalyst resulting from the regenerated catalyst after being tested on stream for 1729 h, as mentioned above, was regenerated for the second time by a different method. The solution of $AlCl_3$ in $CCl_4$ used in the last regeneration method was injected into the reaction. After the catalyst bed had been soaked with the regenerating agent, the temperature was raised to about 75 °C and maintained at that temperature for 24 h. Circulation of the regeneration liquid was not achieved due to lack of the necessary equipment. After the deactivated catalyst had been soaked for 24 h, the temperature was reduced to room temperature. The

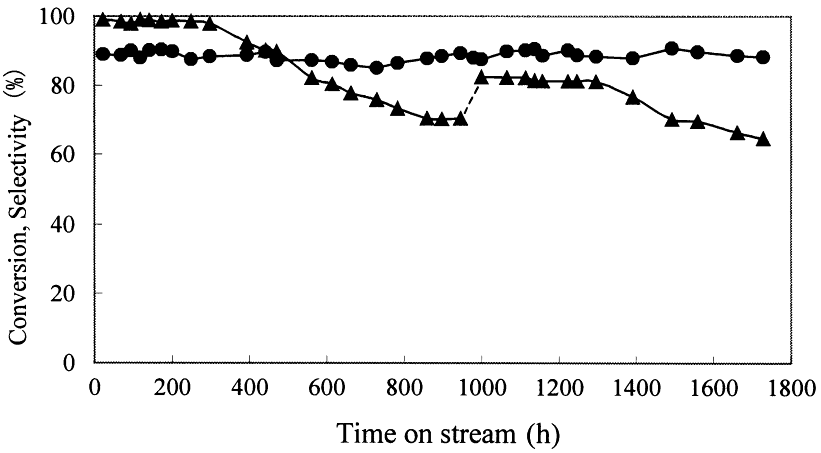

Figure 5. Stability of regenerated (first time) catalyst. Reaction conditions are the same as those in figure 2. ▲, Conversion; ●, selectivity.

reactivated catalyst was washed with dry $CCl_4$ and then flushed with $N_2$ for 1–2 h to remove any remaining $CCl_4$. The catalyst, regenerated twice, showed a conversion of 96% and a selectivity of 90%. No appreciable change in conversion and selectivity was observed after 250 h of continuous running.

The above two methods of regeneration of the deactivated catalyst give satisfactory results. In our work, in which a fixed-bed reactor was used, the second method of regeneration was preferable. The result that the deactivated $AlCl_3$ catalyst immobilized on $\gamma$-$Al_2O_3$ after being regeneration twice still possesses satisfactory catalytic behavior opens up an encouraging prospect for the future application of this catalyst.

## 4. Conclusion

Producing $AlCl_3$ by reacting $CCl_4$ with $\gamma$-$Al_2O_3$ has been shown to be a convenient method of controllably supplying $AlCl_3$ of high purity. Forty-eighty mesh $\gamma$-$Al_2O_3$ having bimodal meso- and macro-pore structure was supposed to be a suitable support for the immobilized $AlCl_3$ catalyst for isobutene polymerization. The amount of $AlCl_3$ immobilized on $\gamma$-$Al_2O_3$ through reaction with hydroxy groups on the surface of $\gamma$-$Al_2O_3$ was 7.5 wt% in terms of $AlCl_x$ ($x = 2.2$). The catalyst showed high activity and selectivity and remarkable stability in isobutene polymerization under mild conditions, as well as nearly perfect reactive specificity to isobutene. Regeneration of the partially deactivated catalyst can be performed by treating with a saturated solution of $AlCl_3$ in $CCl_4$ either *in situ* or *ex situ*. The recovery of activity can be as high as 96% and the regeneration can be done repeatedly.

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