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A study on structural suitability of immobilized aluminum chloride catalyst for isobutene polymerization

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Abstract

Catalytic performance and structural suitability of immobilized $AlCl_3$ catalyst for isobutene polymerization have been studied. It was found that the activity, selectivity and number-average molecular weight of the product polyisobutene depend, to a certain extent, on the pore structure and the granulation of the catalyst. $AlCl_3$ on γ-Al_2O_3 support having macro- and meso-pore bimodal structure show excellent catalytic activity and high stability, while those on γ-Al_2O_3 with micro (d 15.6 Å) and meso-pore (d 28.6 Å) structure exhibit low stability and rapid fall of conversion with time. Granulation of the catalyst is also an important factor which affects activity and selectivity of the catalyst and average molecular weight of the product. Increasing granulation of the catalyst (particles become finer) brings about an increase in isobutene conversion, but a decrease in selectivity, resulting in lower average molecular weight and broader distribution. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: $AlCl_3$; Immobilization; γ-Al_2O_3; Bimodal meso- and macro-pore structure; Isobutene polymerization; Stability

1. Introduction

Immobilization of $AlCl_3$ on solid supports has attracted great attention of researchers in the field of catalysis. So far, most of the works were focused on fixing $AlCl_3$ on commercially often used supports, such as γ-Al_2O_3 [1–3] or SiO_2 [4–6]. There are two main methods for fixing $AlCl_3$ on supports: (1) reacting sublimed $AlCl_3$ with support [1–3,6], and (2) reacting $AlCl_3$ dissolved in CCl_4 or $CHCl_3$ with support [4,5]. Studies on the reaction of the above two methods reveal that $AlCl_3$ is immobilized on the support through reaction between $AlCl_3$ and hydroxy groups on the surface of the support.

A new method of preparing immobilized $AlCl_3$ catalyst on γ-Al_2O_3 has just been reported in our recent paper [7]. In another previous paper on isobutene polymerization over chlorinated γ-Al_2O_3 catalyst [8], we have reported an interesting phenomenon that during the examination of the stability of the catalyst, isobutene conversion gradually decreased with reaction time during continuous reaction, as normally observed for catalytic reaction, however, after an interruption of feeding for a period of 2–3 days, isobutene conversion, which had dropped to a considerable extent, showed remarkable recovery when the feeding was restarted. This phenomena was explained

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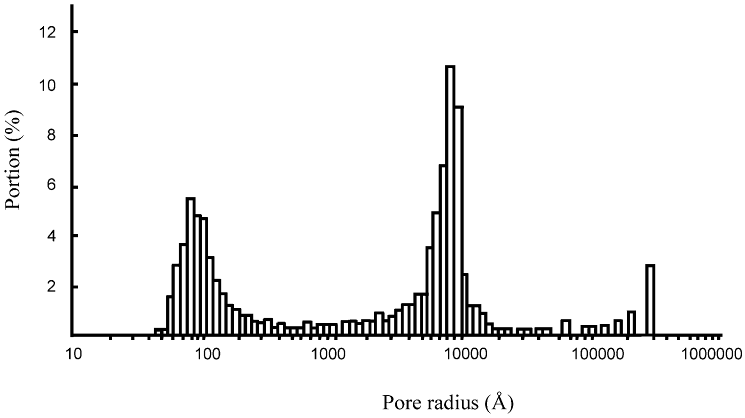

Fig. 1. Pore distribution of A-3 of γ-Al_2O_3.

to be caused by diffusion of higher molecular weight polymer existing in the pore of the catalyst during continuous reaction.

In this paper, the effect of structural characteristics of immobilized $AlCl_3$ catalyst on the polymerization of isobutene was investigated in detail.

2. Experimental

2.1. Materials

Three kinds of γ-Al_2O_3 having micro-pore (average pore diameter (APD), 15.6 Å), meso-pore (APD, 28.6 Å) and bimodal meso- and macro-pore (APD, 1540 Å) structure were used as supports and designated as A-1, A-2 and A-3, respectively. The pore distribution of A-3 is illustrated in Fig. 1. C_4 hydrocarbon mixture was used as a feed for the isobutene polymerization. Its composition is as follows: i-C_4H_8, 27.7 wt.%; 1-C_4H_8, 43.1 wt.%; t-2-C_4H_8, 8.1 wt.%; c-2-C_4H_8, 2.9 wt.%; n-C_4H_{10} + i-C_4H_{10}, 18.2 wt.%.

2.2. Preparation of the catalyst

Forty-eighty mesh (unless specially noted) γ-Al_2O_3 was pretreated at 400°C under N_2 stream for 2 h. $AlCl_3$, which was produced in another reactor by reacting CCl_4 with γ-Al_2O_3 of high purity at 500°C was carried to the reactor containing the pretreated γ-Al_2O_3. The reaction between $AlCl_3$ and γ-Al_2O_3 was allowed to proceed for 4 h at 300°C, then the physically adsorbed $AlCl_3$ was removed by flushing with N_2 at 400°C for 1 h. The reaction product was cooled down to room temperature under N_2 stream.

2.3. Apparatus and procedures

The polymerization reaction of isobutene was carried out in a fixed-bed reactor working at LHSV of $2.0\,h^{-1}$ and under a pressure of 1.0 MPa, which is sufficient to ensure the C_4 hydrocarbon mixture in a liquid state at the reaction temperature. A liquid C_4 mixture containing isobutene was fed to the reactor from an inlet at the bottom of reactor by a syringe pump. The composition of the feed and effluent gas were analyzed with a gas chromatograph (GC). After pretreating the product sample under a pressure of 200 Torr (1 Torr = 133 Pa) and ambient temperature for 30 min, to remove the dissolved C_4 component, W_1 was obtained as the weight of the crude product. W_2 is the weight of the final product, which was further treated under 60 Torr and at 125°C for 1 h to remove isobutene oligomers. 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 by using GC with butanes as an internal standard substance. The average molecular weight ($\overline{Mn}$) and its distribution (D) were determined by a GPC JASCO.

3. Results

3.1. Pore structure of the support and its effect on catalytic properties of the catalyst

Catalysts on supports A-1, A-2 and A-3 are designated as AC-1, AC-2 and AC-3, respectively. The amount of $AlCl_x$ ($x \approx 2.2$) on support was 7.0–7.5 wt.%. The changes of catalytic properties with time on stream over these three catalysts under similar conditions were examined. The result is illustrated in Fig. 2.

From Fig. 2, it can be seen that the three catalysts have very high and comparable initial activity, but they exhibit quite different trend of decrease of activity in the reaction course. AC-1 shows the steepest fall in the activity with time. The conversion falls from 98 to 70% in 150 h and automatically recovers to 87% after 30 h interruption of feeding. The initial conversion of AC-2, which is nearly identical with that of AC-1, falls to 81% after 200 h of running, but the conversion recovers to a value as high as 96% after 30 h interruption of feeding. AC-3 displays the slowest decrease of conversion and can still maintain 94% isobutene conversion after 500 h continuous running.

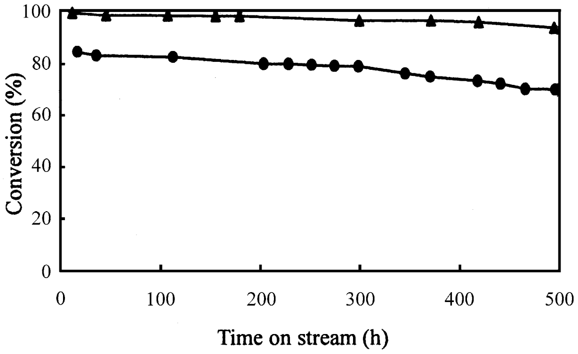

Fig. 3. Comparison of the activity and stability of the catalysts with different size: (●) $\Phi = 1.25$–2.0 mm AC-3; (▲) 40–60 mesh AC-3 (reaction conditions: $T = 30°C$; $P = 1.0$ MPa; LHSV $= 2.0\,h^{-1}$).

3.2. Effect of size of support particles on catalyst properties

The conversion of two AC-3 catalysts prepared from the same support with different particle size (granulation of 40–60 mesh and $\Phi = 1.25$–2.0 mm) were compared. The results are shown in Fig. 3. It is obvious that the catalyst with a diameter of $\Phi = 1.25$–2.0 mm shows much lower conversion than that of those with particle size of 40–60 mesh, decreasing by about 14%

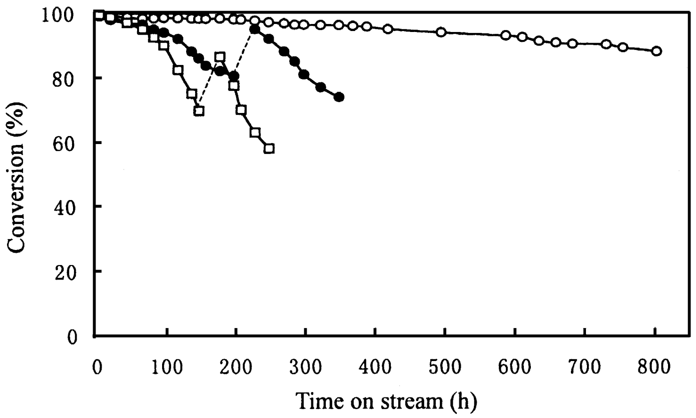

Fig. 2. Change of conversions with time before and after some time of interruption of feeding: (□) AC-1; (●) AC-2; (○) AC-3 (reaction conditions: $T = 32 \pm 1°C$; $P = 1.0$ MPa; LHSV $= 2.0\,h^{-1}$).

Table 1
Effect of granulation of the catalyst on catalytic properties at reaction temperature of 10°C[a]

Granulation (mesh)	Conversion (%)	Selectivity (%)	Average molecular weight of product ($\overline{Mn}$)	Molecular weight distribution (*D*)
80–100	97.8	90.4	1969	2.15
60–80	94.4	94.2	2297	2.10
40–60	81.2	96.0	2472	1.88
20–40	72.3	96.9	2573	1.87
10–20	55.7	97.3	2655	1.85

[a] Reaction conditions: $P = 1.0\,\text{MPa}$, $\text{LHSV} = 2.0\,\text{h}^{-1}$.

Table 2
Effect of granulation of the catalyst on catalytic properties at reaction temperature of 20°C[a]

Granulation (mesh)	Conversion (%)	Selectivity (%)	Average molecular weight of product ($\overline{Mn}$)	Molecular weight distribution (D)
80–100	99.1	87.3	1617	2.21
60–80	96.5	92.6	1831	2.17
40–60	91.0	94.7	1996	1.99
20–40	86.3	95.6	2045	1.94
10–20	67.5	96.3	2102	1.88

[a] Reaction conditions are the same as those in Table 1.

Table 3
Effect of granulation of the catalyst on catalytic properties at reaction temperature of 30°C[a]

Granulation (mesh)	Conversion (%)	Selectivity (%)	Average molecular weight of product ($\overline{Mn}$)	Molecular weight distribution (*D*)
80–100	99.5	81.0	1096	2.32
60–80	97.3	89.1	1257	2.25
40–60	93.7	92.8	1376	2.05
20–40	91.0	93.6	1425	2.01
10–20	77.3	94.3	1510	1.97

[a] Reaction conditions are the same as those in Table 1.

(absolute percentage value). Besides, the 1.25–2.0 mm catalyst exhibits a steeper decrease in conversion. This result clearly illustrates that catalyst on support of coarser particles is inferior in activity and stability to that on support of finer particles.

In order to find out the effect of granulation of a catalyst on its activity and parameters of the product, five kinds of catalysts immobilized on A-3 with five different particle sizes, 100–80, 80–60, 60–40, 40–20, and 20–10 mesh, were made. Their catalytic properties

Table 4
Effect of granulation of the catalyst on catalytic properties at reaction temperature of 40°C[a]

Granulation (mesh)	Conversion (%)	Selectivity (%)	Average molecular weight of product ($\overline{Mn}$)	Molecular weight distribution (*D*)
80–100	100	72.3	891	2.41
60–80	98.1	81.5	970	2.35
40–60	95.4	87.1	1057	2.25
20–40	93.9	89.2	1120	2.15
10–20	84.9	91.2	1150	0.07

[a] Reaction conditions are the same as those in Table 1.

were compared at different temperatures. As shown in Tables 1–4, at a definite temperature, the activity of the catalyst increases with the increase of granulation (i.e. particles become finer) of the support, but the selectivity decreases. At the same time, the average molecular weight of the product becomes lower, and molecular weight distribution becomes broader. While using catalysts of same particle size, their activities increase, while the selectivity decreases with increasing reaction temperature. Meanwhile, the average molecular weight becomes lower and molecular weight distribution broader. These results prove that both granulation of the catalyst and reaction temperature have significant effect on catalytic reaction. The effect of catalyst granulation will be more striking as the reaction temperature becomes lower.

4. Discussion

Isobutene polymerization over immobilized $AlCl_3$ catalyst, like in ordinary heterogeneous catalysis, is influenced by both extraparticle and intraparticle diffusion. Intraparticle diffusion comprises two separate processes: one is the diffusion of reactant molecules from the surface of the catalyst along the pore channel to the interior surface of the catalyst, and the other is the diffusion of product molecules along the pore channel from the interior surface of the catalyst to its exterior surface after desorption. The course of such an intraparticle diffusion depends not only on the properties of the molecules, i.e. their composition, structure, etc., but also on the pore structure and granulation of the catalyst. Eliminating or reducing intraparticle diffusion is crucial in improving activity and stability of the catalyst. In the polymerization of isobutene over three different kinds catalysts, AC-1, AC-2, and AC-3, the difference of change in conversion with time of these catalysts manifests that the smaller the pore diameter, the faster the decrease of conversion and the poorer the stability. The phenomenon of self-recovery of conversion after a period of feeding interruption can be ascribed to "pore-clogging" caused by small amount of large product molecules. On account of the slow rate of diffusion of large molecules, they become accumulated in the pore channel producing "pore-clogging" effect. Thus the substrate isobutene molecules become more and more difficult to have access to the active sites of the catalyst, resulting in a decrease in conversion. Catalyst AC-1, being micro-porous, naturally exhibits steeper drop in conversion than AC-2, which has a meso-porous structure. Self-recovery of conversion after 30 h of interruption of feeding can be attributed to gradual leaving of the large molecules which have clogged the pores. Therefore, the effect of intraparticle diffusion is reduced.

Compared with AC-1 and AC-2, AC-3 shows excellent stability because of their bimodal meso- and macro-pore structure that suits isobutene polymerization. Actually, in AC-3, as shown in Fig. 1, distribution of pores having APD between 120 and 400 Å is 30.0% and APD between 12 000 and 28 000 Å is 43.3%. Besides there is still a population of 8.6% of pores having APD $> 28\,000$ Å. In the bimodal pore structure, meso-pores with their large enough surface area ensures enough number of active sites required for the reaction, whereas macro-pores provide unimpeded exit for the large polyisobutene molecules continually produced to leave the pores with enough rate.

The importance of particle size of immobilized $AlCl_3$ catalyst in the polymerization of isobutene can be seen from the results depicted in Fig. 3. Two kinds of catalysts immobilized on the same material, but differing in size, were used in isobutene polymerization. One is spherical, having diameters of $\Phi = 1.25$–2.0 mm and the other, 40–60 mesh microparticles. The former gives a conversion evidently lower than that of the latter, and shows a faster decrease of conversion with time of reaction. This proves that in the catalytic reaction over the large-sized spherical catalyst, there apparently exists obstruction of intraparticle, increasing granulation of the catalyst is one of the effective methods of eliminating intraparticle diffusion.

Difference in granulation can produce deep effects on conversion, selectivity, average molecular weight and distribution of the product (Tables 1–4). These results show that the lower the temperature, the more noticeable the difference in above-mentioned properties caused by the change in granulation of the catalyst. As the catalyst particles become finer, the intraparticle diffusion in pores of the catalyst becomes easier, and hence the time of stagnation of the product molecules in the pores of the catalyst become shorter. From the above reason, the results of the increase in the activity and the decrease in the selectivity with the increase of the granulation were clearly elucidated.

One of the important characteristics of immobilized $AlCl_3$ catalyst in the polymerization of isobutene is that the molecular weight distribution is comparatively narrow. When the reaction temperature is within the range 10–40°C, the molecular weight distribution of products is 2.1 ± 0.3, which is much narrower than that observed in traditional technology of using $AlCl_3$ as catalyst (generally between 2.5 and 3.0).

5. Conclusion

In the polymerization of isobutene, immobilized $AlCl_3$ catalysts, made from micro-pores (APD 15.6 Å) and meso-pore (APD 28.6 Å) γ-Al_2O_3 supports, show poor stability. The main reason is "pore-clogging" effect caused by the stagnation of large polyisobutene molecules within the pore channel of the catalyst, i.e. the harmful influence of intraparticle diffusion. When γ-Al_2O_3 having a bimodal meso- and macro-pore structure is used as the support, intraparticle diffusion in the catalyst can be effectively reduced, resulting in a remarkable enhancement of the stability of the catalyst. Granulation of the catalyst is another important factor. Increase of granulation of the catalyst causes an increase in conversion, but a decrease in selectivity, and at the same time a lowering of the average molecular weight and broadening of product distribution. Therefore, particle size effect may be ascribed to similar reason, i.e., reducing staying time of large molecule in product within pore channel.

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