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Influence of Geometric Structure of Immobilized Aluminium Chloride Catalyst on Catalytic Property in Isobutene Polymerization

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Abstract: The catalytic property of $AlCl_3$ catalyst immobilized on γ-Al_2O_3 for isobutene polymerization has been studied. It was found that the activity, selectivity and stability of the catalyst are dependent greatly on geometric characteristic of the pore structure and size of catalyst. Although the activity and selectivity of the catalysts with micro- and meso-pore structure are all high in initial stage, but their stability is low, while those with bimodal meso- and macro-pore structure are excellent. Increasing granularity of the catalyst (particle become fine) brings about an increase in isobutene conversion, but a decrease in selectivity, resulting in lower average molecular weight and its broader distribution.

Keywords: $AlCl_3$ immobilization, γ-Al_2O_3, bimodal meso- and macro-pore structure, isobutene polymerization, stability

$AlCl_3$ is one of the most important and widely used Friedel-Crafts catalysts. As a catalyst, it has serious drawbacks. Besides being corrosive, it also causes other troubles, such as difficulty to separate from products and production of large amounts of environment-polluting waste, which have increasingly hindered its successful application in chemical and related industries. Scientists have been striving for a long time to change $AlCl_3$ into an environmentally friendly catalyst through immobilization on a suitable support[1~6]. Our research group, after many years effort, have successfully developed γ-Al_2O_3 supported $AlCl_3$ catalyst which can be used in polymerization of isobutene in C_4 hydrocarbon mixture. Structural characteristics, being of utmost importance to the activity of this catalyst, will be discussed in this paper.

Experimental

Three kinds of γ-Al_2O_3 were selected as the support. The first kind（A-1）, having an average pore diameter of 15.6 Å is microporous γ-Al_2O_3; the second kind（A-2）is mesoporous γ-Al_2O_3 with an average diameter of 28.6 Å. The third kind（A-3）is mainly bimodal meso- and macro-porous with an average diameter of 15840 Å. Its total degree of porosity is 87.2 v.%, mainly distributed among pores with diameters in the 120~400 Å range（30%）and in the 12000~28000 Å range（43.3%）. Besides, there is still 8.6% of pores with an average diameter ＞280000 Å. The catalysts made from A-1, A-2 and

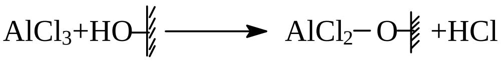
A-3 are numbered AC-1, AC-2 and AC-3, respectively.

Catalysts were prepared through a two-step method. In the first-reactor, CCl_4 was made to react with highly pure γ-Al_2O_3 at 500°C to form $AlCl_3$, the $AlCl_3$ formed was then carried by N_2 into the second reactor, containing the support γ-Al_2O_3 which had been pretreated at 400°C, $AlCl_3$ and γ-Al_2O_3 were allowed to react at 300°C for 4 h. The product was then flushed at 400°C for 1 h and finally cooled in N_2 to room temperature.

Selective polymerization of isobutene fraction was carried out in a fixed bed reactor under a pressure of 1.0 MPa. The raw material containing 27.7% isobutene was fed from the bottom of the reactor by a syringe pump. After the pressure being reduced to ordinary pressure by a back-pressure regulator, gaseous constituent of the feed was separated from the liquid product by means of a gas-liquid separator. Raw material and effluent gas were analyzed by GC, molecular weight of the products and their distribution were determined by GPC.

Results and discussion

Immobilization of $AlCl_3$ is accomplished through its reaction with the hydroxyl groups on the surface of γ-Al_2O_3, which can be expressed as follows:



$$AlCl_3 + HO- \longrightarrow AlCl_2-O- + HCl$$

The amount of $AlCl_x$ in the catalyst AC-3 is about 7.5 wt.%; x=2.2.

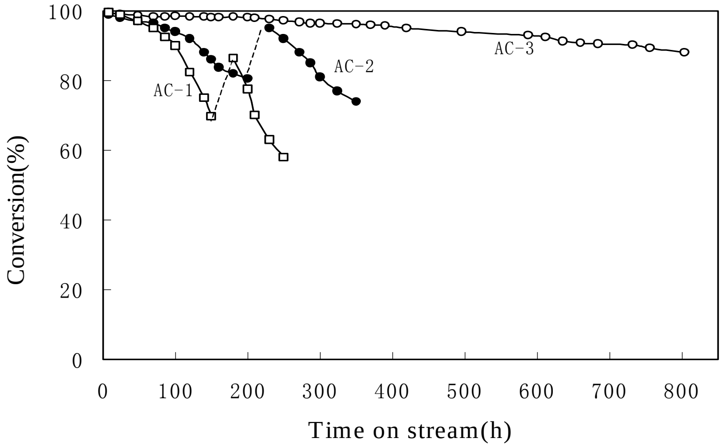
The catalytic behavior of immobilized $AlCl_3$ catalyst for isobutene polymerization depends largely on the structural characteristics of the catalyst, mainly pore structure and particle size.

Pore plugging and its origin

The change of catalytic activity with reaction time of the three immobilized $AlCl_3$ catalyst with 40~60 meshes AC-1, AC-2 and AC-3 were examined under identical conditions. Results are depicted in **Figure.1**.

From **Figure 1**, it can be seen that catalytic activity of both microporous AC-1 and mesoporous AC-2 show rapid fall with reaction time. 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 conversion of AC-2, the initial conversion of 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% through 30 h cessation of feeding. Compared with AC-1 and AC-2, AC-3 exhibits high stability in activity, maintaining a conversion over 90% even after 800 h of continuous running. The rapid fall of activity with AC-1 and AC-2 might be due to the slowing down of diffusion rate of macromolecules of polybutenes formed in course of reaction. When the average molecular weight of the polymer, $\overline{Mn}$, reaches to around 2000, the percentage of large molecules having molecular weight $>$10000 amounts reaches to 4~10%. Slow diffusion rate of macromolecules causes "pore plugging", thereby seriously affects conversion. It appears that the smaller the pore diameter, the greater the pore plugging effect. AC-3 possesses bimodal meso- and macro-pore structure and macropores in which providing channel for the massive product molecules to diffuse. Structurally, AC-3 is the most favorable catalyst for the polymerization of isobutene.

Figure 1 Variation in the polymerization conversions of the catalysts with increasing of time on stream

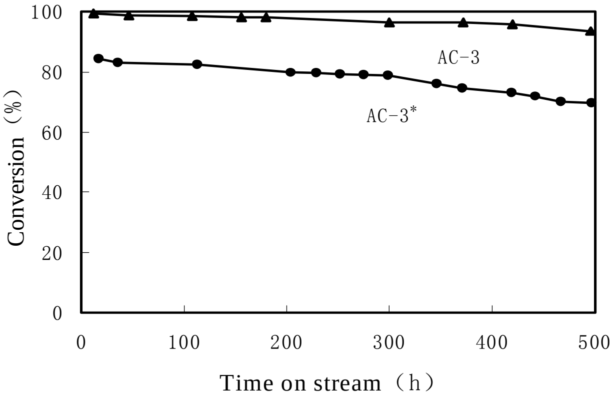


Reaction conditions: T=32±1°C, P=1.0 MPa, LHSV=2 h^{-1}

Effect of size of catalyst particle

A comparison of catalytic activity was made between two catalysts AC-3 and AC-3*, made from the same γ-Al_2O_3 containing both meso- and macropores. But they differ in particle size. The former has a granulation of 40~60 mesh, which showed good stability of the catalytic activity,

Figure 2 Comparison of the activity and stability of the catalysts with different size



Reaction conditions: T=30°C, P=1.0 MPa, LHSV=2.0 h^{-1}

while the latter has particle diameters in the 1.25~2.0 mm range, latter shows considerably lower activity and stability than that of the former. After 500 h of continuous running, in the case of latter, the conversion drops from an initial 80% to 72% as shown in **Figure 2**. It can evidently be seen that the catalyst AC-4 gives a conversion of 14% (absolute percentage value) lower than AC-3. Besides, the latter displays a steeper decrease in conversion. This result forcibly illustrates that catalyst on supports of coarse particles are inferior in activity and stability to those on supports of finer particles.

In this work, difference in activity of 5 groups of the catalyst having granulation of 100~80 mesh, 80~60 mesh, 60~40 mesh, 40~20 mesh and 20~10 mesh was examined. Results of 1 set of experiments are given the following **Table 1**.

Table 1 shows that when the size of catalyst particle increases, conversion decreases, selectivity increases, meanwhile $\overline{Mn}$ becomes greater and molecular distribution becomes narrower. Above particle size effect may be ascribed to change of stay time of product molecules in pore channel. This result clearly manifest the effect of intraparticle diffusion on the proceeding of catalytic process.

Table 1 Effect of granularity of catalyst particles

Granulation (mesh)	Conv. (%)	Selec. (%)	Aver. mol.wt. of product	Mol.wt. distribution
100~80	97.8	90.4	1969	2.15
80~60	94.4	94.2	2297	2.10
60~40	81.2	96.0	2472	1.88
40~20	72.4	96.9	2573	1.87
20~10	55.7	97.3	2655	1.85

Reaction condition: T=10°C, P = 1.0 MPa, LHSV=2.0 h^{-1}

Conclusion

In the polymerization of isobutene, immobilized $AlCl_3$ catalysts, made from micro- or meso-pore structure γ-Al_2O_3, showed poor stability, while the catalyst with bimodal meso- and macro-pore structure displayed excellent stability. Decrease in particle size increases both stability and activity of the catalyst. Our highly reactive catalyst having average pore diameter of *ca.* 15000 Å and granulation of 40~100 mesh, gives a satisfactory product polyisobutene with a molecular weight range 2400~2000.

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