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Comparison of ethylene polymerization catalyzed over Cr(VI)/silica and Cr(II)/silica catalysts

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Summary

Ethylene polymerization and the morphology of produced high density polyethylene (HDPE) catalyzed over Cr(VI)/silica and Cr(II)/silica were studied. Cr/silica catalyst with Cr loading of 1 wt % has been prepared by impregnating an aqueous solution of CrO_3 onto silica having specific surface area of 301 m^2/g and pore volume of 1.64 ml/g. The rate profiles and the morphologies of polyethylene polymerized over Cr(VI) and Cr(II)/silica were different. The process of active site formation influences the rate profiles. The shape of polyethylene particles polymerized with Cr(II)/silica resembled the original shape of catalyst particles. However, Cr(VI)/silica catalyst particles were fractured inhomogeneously during the polymerization. The variation of molecular weight and molecular weight distribution at various polymerization times indicated that the formation of active sites of Cr(VI)/silica was accomplished gradually during polymerization.

Introduction

Owing to its commercial importance, Phillips Cr/silica ethylene polymerization catalyst has been subjected to an extensive investigation. Many of these investigations were concerned with the nature and identification of the catalytically active species and polymerization mechanism (1).

Ethylene polymerization with Cr/silica was investigated extensively. However, most of them were conducted at room temperature and low pressures below 1 atm. However, the polymerization data at low pressures do not apply to the commercial polymerization condition because the polymerization rate is dependent on the pressure and temperature. Even in the polymerization studies under commercial conditions, the differences in the polymerization behaviours catalyzed over Cr(VI)/silica and Cr(II)/silica catalysts were not clearly understood. However, it has been reported without detail investigations that polyethylene produced by Cr(II)/silica was almost identical to that produced by Cr(VI)/silica (1,2).

In this paper we have studied the ethylene polymerization behaviours of Cr(VI)/silica and Cr(II)/silica at the commercial operating conditions. The variation in the rate profiles, morphology of polyethylene produced, and formation of active sites during polymerization were discussed.

Experimental

Catalyst preparation.

Cr/silica catalyst was prepared by impregnating an aqueous solution of CrO_3 onto the silica

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(from Strem Chem. Co.). The silica was suspended in a relatively large amount of solution and the suspension was dried in a rotary evaporator for about 10 hr. During this procedure the temperature did not exceed 323 K. Catalyst was further dried in oven at 380 K for 12 hr. The resulting catalyst contains 1.0 wt % chromium.

To obtain the Cr(VI)/silica, fresh catalyst was activated by calcining with dry air. A fluidized bed was slowly raised to 1123 K over 2 hr, and then held at 1123 K for another 2 hr. After activation the sample was purged with dry nitrogen at 623 K for 0.5 hr and then cooled down to room temperature under nitrogen to avoid adsorption of oxygen during cooling. To obtain the Cr(II)/silica, the activated catalyst, Cr(VI)/silica, was reduced in a fluidized bed with CO at 623 K for 0.5 hr. All the gases were predried through activated alumina and 5A type molecular sieve column. CO was also deoxygenated through Ridox (Fischer Sci. Co.) column.

Polymerization.

Ethylene polymerization was carried out at 378 K in a 2-liter stirred autoclave without any cocatalyst such as AlR_3. A pressurized jacket filled with boiling methanol was used to control the internal temperature of the reactor at 378 K within 0.5 K. 50 to 80 mg of Cr(VI)/silica or Cr(II)/silica were charged under dry nitrogen. Then 1 liter of liquid isobutane diluent was charged. Ethylene was introduced to the autoclave to maintain the polymerization pressure at 550 psig. The rate of polymerization was measured by monitoring the ethylene flow with mass flow meter. Isobutane and ethylene were purified through activated alumina and Ridox column.

Results and discussion

Rate profile and morphology.

The summary of ethylene polymerization experiment is listed in Table 1. Ethylene polymerization was stopped at the catalytic productivity of 500, 1500, and 3000 gPE per gram catalyst to compare the properties of polyethylenes at each productivity. The typical rate profiles of ethylene polymerization with time are shown in Fig. 1.

Table 1. Summary of ethylene polymerization over Cr(VI) and Cr(II)/silica catalyst.

Run #	Catalyst	Catalyst amount (mg)	Induction Time (min)	Productivity (gPE/gCat.)
1.	Cr(VI)	59	5.7	3000
2.	Cr(VI)	51	5.8	1500
3.	Cr(VI)	68	5.6	500
4.	Cr(II)	50	0	3000
5.	Cr(II)	66	0	1500
6.	Cr(II)	76	0	500

Cr(VI)/silica was not immediately active upon introduction of ethylene into the reactor, but had an induction time of 5-6 min. This is thought to be due to the slow initial reduction of Cr(VI) by ethylene to the Cr(II) active site, or to the desorption of poisonous by-products such as formaldehyde (3-5). The polymerization rate catalyzed over Cr(VI)/silica gradually increased after induction time. This might be due to the increase in the number of active sites during polymerization. Zakharov and Ermakov reported that the increase in the reaction rate of Cr(VI)/silica was due to the increase in the number of propagation centers measured by the radio tracer technique during polymerization, but whether this increase in the number of propagation centers was caused by fragmentation or chemical change in the catalytically active species was not discussed (6).

The scanning electron micrograph of Cr(VI)/silica activated at 1123 K as shown in Fig. 2 is compared with those of polyethylenes at different catalytic productivities of 500, 1500, and 3000 gPE/g-catalyst as shown in Fig. 3. The shape of polyethylene particles produced by Cr(VI)/silica did not resemble those of catalyst particles, which were fractured inhomogeneously as shown in Fig. 3(a), (b), and (c). McDaniel also reported that Cr(VI)/silica catalyst was fractured during ethylene polymerization (7). He concluded that fragmentation was complete within the first few minutes of polymerization and was not rate-controlling step (7). Therefore, it can be explained that the gradual increase in the polymerization rate of Cr(VI)/silica is due to the chemical change of catalytically active species. In other words all of Cr(VI) species can not be reduced by ethylene to catalytically active Cr(II) at the same time, but reduced gradually during polymerization.

Cr(II)/silica did not show any induction time, but showed a high polymerization rate immediately after exposure to ethylene as shown in Fig. 1. However, the polymerization rate decreased gradually during the polymerization after 10 min. Although Cr(II) sites were already formed by prereducing the Cr(VI) to Cr(II) with CO at 623 K, this catalyst showed a gradual rise in activity upto 10 min. This might be due to a slow initiation reaction in

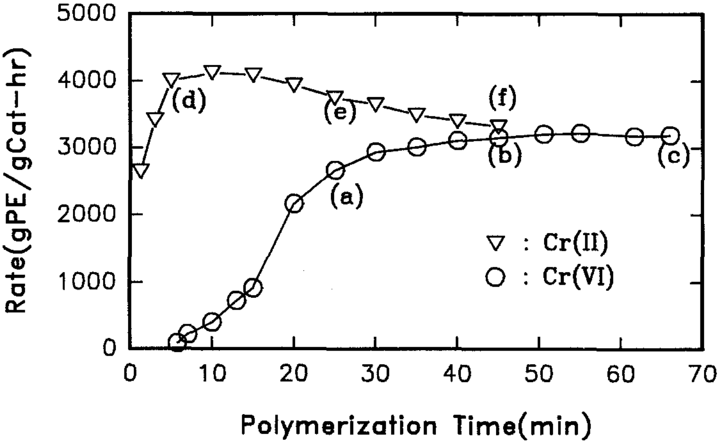


Figure 1. Rate profiles of ethylene polymerization over Cr(VI) and Cr(II)/silica catalyst. Polymerization condition: T= 378 K, P_{tot}= 550 psig. (a), (b), (c), (d), (e), and (f) indicate the polymerization time of scanning electron micrographs as shown in Fig. 3.

which the active sites are initiated by ethylene. The incorporation of the first ethylene to Cr(II) is poorly understood, and might be slower than the incorporation of succeeding monomer. Merryfield et al. reported that the gradual increase in the polymerization rate may be due to a slow initiation reaction and that the polymerization rate increased with polymerization time contrary to our result (2).

In the case of Cr(II)/silica, the shape of polyethylene particles at the polymer productivity of 500 gPE/g-catalyst is spherical similar to that of catalyst particles as shown in Fig. 2 and Fig. 3(d). As the polymer productivity of Cr(II)/silica increased to 1500 and 3000 gPE/g-catalyst, polyethylene particles are still spherical as shown in Fig. 3(e) and (f).

Two explanations for the decrease in the polymerization rate of Cr(II)/silica after 10 min come to mind: (1) polymer build-up around the catalyst particle physically retards diffusion of ethylene to the active sites; or (2) the active site undergo some chemical change. The first possibility seems likely because the catalyst fragments were encaptulated by polyethylene. If this diffusion limitations through the polyethylene film encapsulating catalyst fragments results in the decrease in the apparent polymerization rate with the Cr(II)/silica, polydispersity index (PDI) of polymer produced must increase with catalytic productivity. However, PDI of polyethylene polymerized over Cr(II)/silica decreased with catalytic productivity as shown in Fig. 4. This confirms that the decay is not due to diffusion limitation. Instead the second explanation seems more probable, that some of active sites are chemically unstable, or become poisoned during polymerization. It was reported from the studies of oxygen chemisorption, chemiluminescence, and ir spectroscopy that the different types of active site were formed after reduction of Cr(VI) species to Cr(II) species (9-12).

Molecular weight, molecular weight distribution, and density of produced polyethylene

The weight average molecular weights and polydispersity index (PDI) of polyethylene produced at the different polymer productivities are shown in Fig. 4. Molecular weight slightly increased and did not change much with the polymerization time. The molecular weight of polyethylene prepared with Cr(II)/silica was higher than that of polyethylene prepared with Cr(VI)/silica.

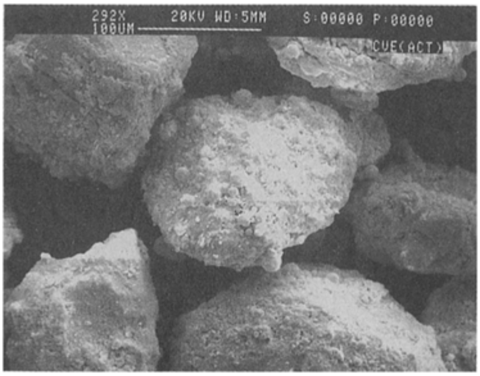
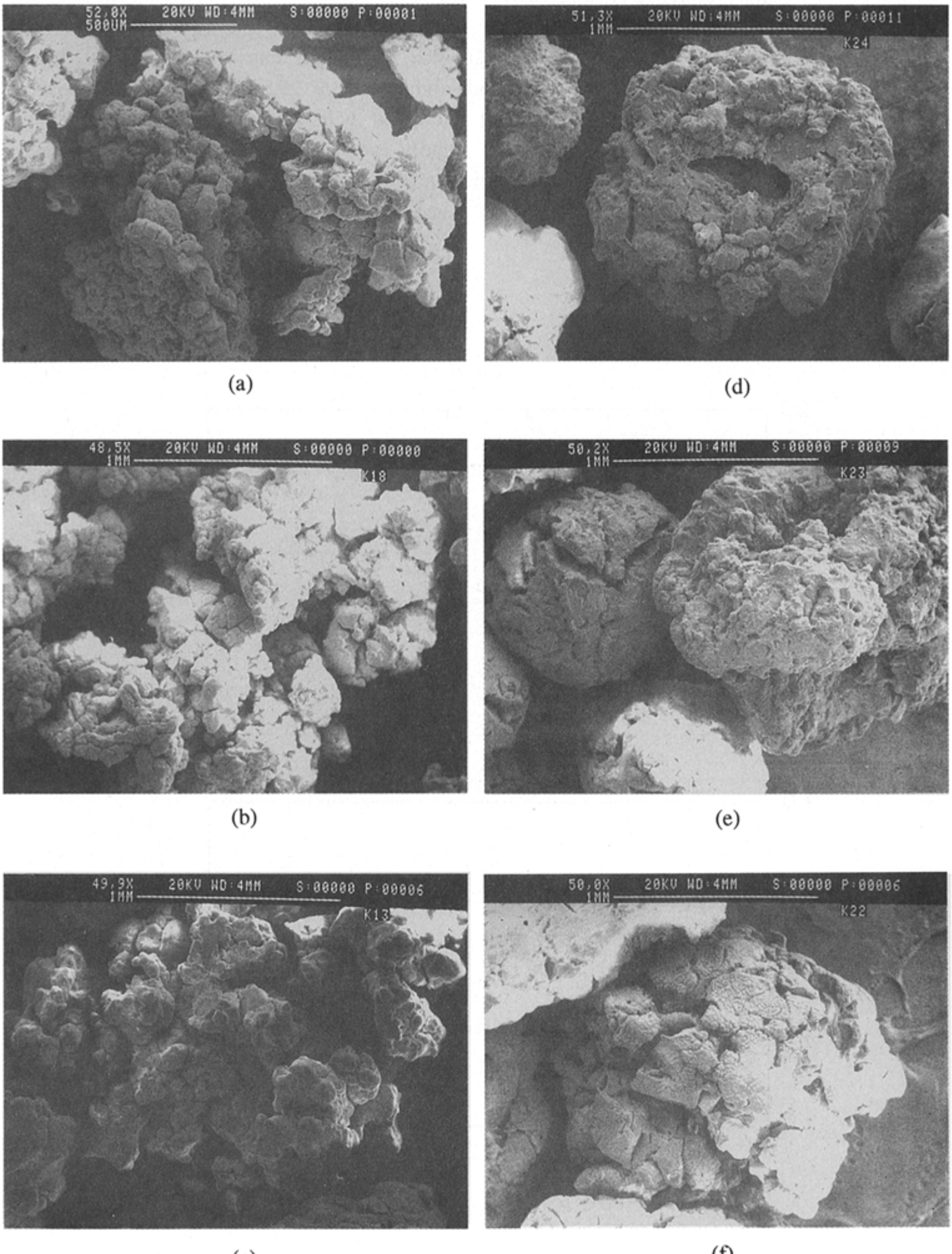


Figure 2. Scanning electron micrograph of catalyst activated with dry air at 1123 K.



(a) (d)

(b) (e)

(c) (f)

Figure 3. Scanning electron micrographs of polyethylenes polymerized with Cr(VI)/silica and Cr(II)/silica catalyst. (a), (b), and (c) for Cr(VI)/silica, and (d), (e), and (f) for Cr(II)/silica at the productivity of 500, 1500, and 3000 gPE/gCat, respectively.

The heterogeneous nature of active sites of Cr(II)/silica is responsible to have different molecular weight and molecular weight distributions.

The PDI of polyethylene produced with Cr(II)/silica was larger than that of polyethylene produced with Cr(VI)/silica at the polymer productivity of 500 gPE/g-catalyst. However, PDI of polyethylene produced with Cr(II)/silica decreased with polymerization time, while PDI of polyethylene produced with Cr(VI)/silica slightly increased with polymerization time. The PDI of polyethylene produced with Cr(II)/silica larger than that of polyethylene produced with Cr(VI)/silica can be explained by the more heterogeneous nature of the active sites of the former.

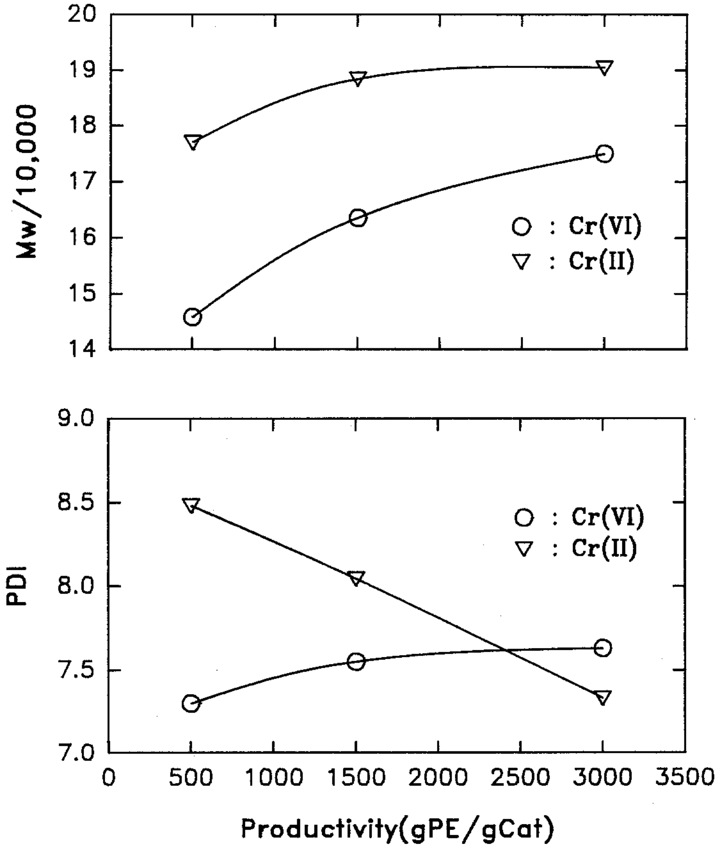


Figure 4. Effect of catalyst productivity on the weight average molecular weight (Mw) and polydispersity index (PDI) of polyethylene produced.

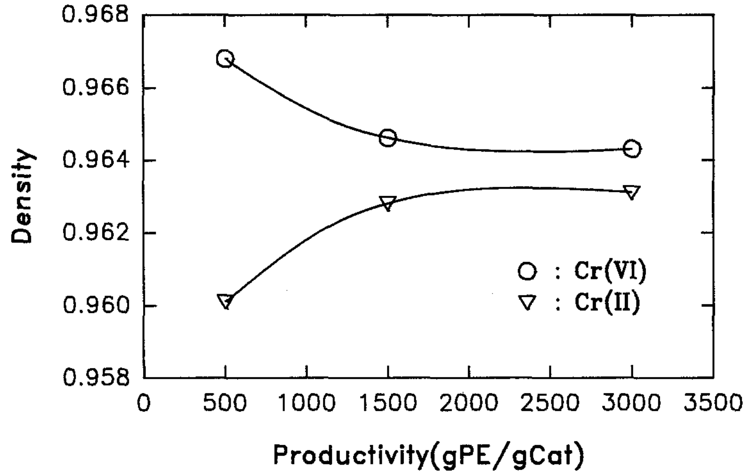


Figure 5. Effect of catalyst productivity on the density of polyethylene produced by Cr(VI)/silica and Cr(II)/silica.

The PDI of polyethylene produced with Cr(VI)/silica slightly increased with polymerization time indicating that inhomogeneity of the active sites increased due to the formation of new type of Cr(II) species by the reduction with ethylene.

The density of polyethylene produced with Cr(II)/silica increased with polymerization time and is less than that of polyethylene produced with Cr(VI)/silica as shown in Fig. 5. The density of polyethylene produced with Cr(VI)/silica decreased with polymerization time. This indicates that the differences in the active sites and the mode of catalyst fragmentation also affect the crystallization of polyethylene chain segments.

Conclusion

The polymerization rate catalyzed over Cr(VI)/silica gradually increased after induction time due to the gradual reduction of Cr(VI) to catalytically active Cr(II) species. Cr(II)/silica does not show any induction time, but shows a high initial polymerization rate because all of active sites were already formed by prereducing Cr(VI)/silica with CO. The morphology, molecular weight and molecular weight distribution of polyethylene produced are dependent on the types of active sites and the mode of fragmentation of catalyst particles. Replication phenomenon was observed for Cr(II)/silica, while Cr(VI)/silica did not show any replication phenomenon.

Acknowledgement

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