

Ethylene polymerization with Cp_2ZrCl_2 supported on dealuminated Y zeolite

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Summary

Y zeolites with different aluminium contents obtained by dealumination with ammonium hexafluorosilicate were evaluated as supports for bis(cyclopentadienyl)-zirconium dichloride catalysts. The activities of the supported and homogeneous systems were compared for ethylene polymerization. The most active heterogeneous catalyst was the one supported on the zeolite with the higher Si/Al ratio and external area.

Introduction

Homogeneous metallocene/MAO catalyst systems for polyolefin synthesis have high activities and produce polymers with narrow polydispersities and excellent stereocontrol. From the point of view of practical application, they have some drawbacks since modern gas phase polymerization processes require heterogeneous catalysts. By supporting the metallocene compound on a suitable material a combination of the catalyst properties with the control of polymer morphology could be achieved (1 - 4).

The use of zeolites as catalyst support for metallocene is an interesting option, due to the high surface areas of these materials. Zeolites are crystalline aluminosilicates formed by a tridimensional network of TO_4 tetrahedra, where T is usually silicium or aluminium. These tetrahedra are linked to each other by sharing the oxygens atoms, forming a framework that presents pores and/or cavities of molecular dimensions. The zeolite framework presents negative charges due to the trivalent aluminium atoms that are counterbalanced by extra-framework cations having high mobility and which can be ion-exchanged. The various types of zeolites differ from each other by their chemical composition and by the topology of their tridimensional structure. Y zeolite is a synthetic faujasite type zeolite presenting supercages of about 13 Å formed by the interception of channels of about 7.5 Å in diameter in a tridimensional array.

In a recent work (5,6) Y and MOR (mordenite) zeolites were tested as supports for Cp_2ZrCl_2 and it was concluded that the concentration of framework aluminium atoms is the dominant factor, but that the contribution of the external surface is also important since the access of the catalyst to the micropores of the support seems to be limited.

To check this hypothesis, in this work a NaNH_4Y zeolite was gradually dealuminated with ammonium hexafluorosilicate ($(\text{NH}_4)_2\text{SiF}_6$ or HFS) aiming at preparing samples with different Si/Al framework ratios and textural characteristics. These materials

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were used, with or without prior treatment with MAO, as supports for Cp_2ZrCl_2 . These heterogeneous catalysts were evaluated in ethylene polymerization.

Experimental part

Materials

A NaNH_4Y , synthesized according to Ferreira (6), with an overall Si/Al ratio of 2.5 and a sodium content close to 3% was used as precursor. Cp_2ZrCl_2 was used as received from Wako Pure Chemical Industry Ltd. Methyl aluminoxane (MAO) (donated by Witco as a 30% w/w toluene solution) was also used as received. Toluene was purified by refluxing and freshly distilled under nitrogen from a Na/benzophenone system. Nitrogen was deoxygenated and dried by passing through columns of Cu catalyst and of activated molecular sieve (4Å), respectively. Polymerization-grade ethylene (donated by CENPES-Petrobrás) was dried by passing through columns of activated molecular sieves (4Å).

Support preparation

NaNH_4Y zeolite was suspended in an aqueous ammonium acetate solution (pH = 6-7) and then treated with a 0.75M $(\text{NH}_4)_2\text{SiF}_6$ solution at 85°C according to Cruz et al. (8). The HFS/zeolite mass ratio and the reaction time were varied as shown in Table 1. The zeolites were recovered by filtration, repeatedly washed with boiling water and finally dried in an oven at 110°C.

Table 1: Support preparation

| Support # | $(\text{NH}_4)_2\text{SiF}_6$ / zeolite (w/w) | Reaction time (min) |
|-----------|---|---------------------|
| YHFS-01 | 0.1 | 45 |
| YHFS-02 | 0.1 | 180 |
| YHFS-03 | 0.3 | 180 |
| YHFS-04 | 0.5 | 180 |

Prior to catalyst preparation, the zeolites were calcined under controlled conditions (2°C/min, 2 h at 300°C, under N_2 flow) to eliminate the adsorbed water and to decompose the ammonium ions. Subsequently, the samples were cooled and stored under dry N_2 .

Support characterization

The zeolite composition was determined by atomic absorption spectrometry (AAS) in a Perkin Elmer 1100B spectrometer. The framework silica to alumina ratio (SAR) and the presence of extra-framework aluminium species were determined by Si^{29} and Al^{27} MAS/NMR, in a Varian VRX-300 FT-NMR spectrometer. The textural characterization of the zeolites was carried out by N_2 adsorption at -196°C in a Micromeritics ASAP 2000.

Catalyst preparation

Operations were carried out under nitrogen using Schlenk techniques. Two series of catalysts were prepared:

- S01 series: Cp_2ZrCl_2 ($[\text{Zr}] = 0.05$ mmol/g zeolite) was immobilized on the support under reflux for 8 h.
- S02 series: zeolites were pre-treated with MAO ($[\text{Al}] = 2.5$ mmol/g zeolite) at 50°C for 4h and then washed with toluene at 90°C . Then Cp_2ZrCl_2 was added under the same conditions described for the S01 series.

Ethylene polymerization

Ethylene polymerizations were carried out at 50°C for 1 h at 100 mm Hg of monomer pressure in a 250 mL round-bottom glass flask equipped with a mechanical stirrer and gas inlets. The concentration of Zr in the reaction medium was 0.005 mmol/100 mL toluene and the Al/Zr ratio was 2000. Acidified methanol was added to interrupt the reaction after 1h. The polymer was filtered, washed with methanol and dried at 60°C to constant weight.

Polymer characterization

The weight-average molecular weight (M_w) and molecular weight distribution (M_w/M_n) were determined by gel-permeation chromatography (GPC) using a Waters 150CV-Plus chromatograph at 135°C and 1,2,4-trichlorobenzene solutions, calibrated with standard polystyrenes.

Results and Discussion

Table 2 presents the specific area and pore volume of the dealuminated zeolites determined by N_2 adsorption.

Table 2: Textural characteristics of the zeolites

| Characteristic | NaNH_4Y | YHFS-01 | YHFS-02 | YHFS-03 | YHFS-04 |
|---|-------------------------|---------|---------|---------|---------|
| S_{BET} (m^2/g) | 732 | 713 | 734 | 606 | 381 |
| $S_{\text{external}}^{(a)}$ (m^2/g) | 13 | 12 | 12 | 14 | 22 |
| $V_{\text{micropore}}^{(a)}$ (cm^3/g) | 0.34 | 0.33 | 0.34 | 0.28 | 0.17 |
| $V_{\text{mesopore}}^{(b)}$ (cm^3/g) | 0.025 | 0.043 | 0.035 | 0.064 | 0.15 |

(a) t-plot

(b) BJH method - 20 - 600Å

The results show that YHFS-01 and YHFS-02 exhibit virtually no differences in textural characteristics, as compared to the parent zeolite. In contrast, more severe treatments affected the porous structure of the samples significantly. The sharp decrease of the microporosity of YHFS-04 and the corresponding increase in its mesoporosity suggests that this sample was highly dealuminated and that part of its crystalline structure has been destroyed.

The results of characterization by atomic absorption spectroscopy and by Al^{27} and Si^{29} NMR spectroscopy are shown in Table 3.

Table 3: Chemical Characteristics of the Zeolites

| Support # | Na (%) | Si/Al ratio | | | % EFAL* Al ²⁷ NMR |
|---------------------|--------|-------------|--------------------------------|--------------------------------|---------------------------------|
| | | Global AAS | Framework Si ²⁹ NMR | Framework Al ²⁷ NMR | |
| NaNH ₄ Y | 3.0 | 2.5 | 2.4 | 2.5 | 0 |
| YHFS-01 | 2.0 | 2.6 | 2.6 | 2.6 | 0 |
| YHFS-02 | 1.9 | 2.7 | 2.8 | 2.7 | 0 |
| YHFS-03 | 1.9 | 3.5 | 3.9 | 3.7 | 6.5 |
| YHFS-04 | 1.8 | 4.5 | 4.9 | 6.4 | 30 |

*% EFAL: % of aluminium in octahedral coordination

It can be seen that by increasing the reaction time and, specifically, the (NH₄)₂SiF₆/zeolite ratio, the removal of aluminium framework increases. In agreement with the data from textural characterization, the chemical analyses of YHFS-03 and YHFS-04 indicate that significant dealumination has occurred and that extraframework aluminium species were not completely washed out from these samples.

The polymerization results using these materials as supports for the metallocene catalyst are shown in Table 4.

Table 4: Polyethylene Synthesis

| Catalyst # | Catalytic Activity (kg PE/mol Zr.h) | Mw.10 ⁻⁵ | Mw/Mn |
|-----------------------------------|--|---------------------|-------|
| Cp ₂ ZrCl ₂ | 1684 | 2.49 | 1.9 |
| YHFS-01-S01 | 24 | 9.07 | 1.7 |
| YHFS-01-S02 | 268 | 7.74 | 2.1 |
| YHFS-02-S01 | 112 | 7.53 | 1.9 |
| YHFS-02-S02 | 14 | 4.29 | 1.7 |
| YHFS-03-S01 | 346 | 5.98 | 1.8 |
| YHFS-03-S02 | 540 | 8.27 | 2.0 |
| YHFS-04-S01 | 1232 | 8.14 | 1.9 |
| YHFS-04-S02 | 562 | 6.16 | 2.5 |

Those results show that although the supported catalysts were not as active as the homogeneous ones, they produced higher molecular weight polymers and that the

molecular weight distributions were equally narrow. The results of the S02 catalyst series (with prior treatment of the support with MAO) shows random behavior which may be due to difficulties in washing out the excess (non fixed) MAO from the support.

The most active catalyst was that supported on YHFS-04. This support presented not only the smallest specific area and micropore volume but also extraframework aluminium species blocking, at least partially, the access to the interior of the pore system. In agreement with our previously reported results (5), this result indicates that the contribution of the internal area is not significant. This is consistent with the relatively large dimensions of the Cp_2ZrCl_2 molecule. The results also indicate that the increase of the Si/Al framework ratio of the support affected catalyst performance. Particularly for the catalyst supported on YHFS-04, series 01, the slight loss of activity as compared to the homogeneous system was counterbalanced by an increase of the polymer molecular weight. Work is in progress to improve MAO fixation conditions.

Conclusions

Zeolite-supported Cp_2ZrCl_2 catalysts were prepared and evaluated for ethylene polymerization. These systems produced polyethylene with higher molecular weight and as narrow a molecular weight distribution as the homogeneous precursor, however, at relatively lower activity.

The main characteristic that makes a zeolite a good support for metallocene catalyst seems to be a high Si/Al value and therefore a low Al density on the surface of the zeolite. This suggests that the presence of isolated aluminium atoms favors the fixation of zirconocene.

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