

ZSM-5 acid zeolite supported metallocene catalysts for ethylene polymerization

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Abstract

Zeolite H-ZSM-5 was used as support for the impregnation of Cp_2ZrCl_2 catalyst in the synthesis of polyethylene. The catalyst preparation conditions were varied and the statistic program was employed with the purpose of evaluating the best catalyst preparation method.

In order to utilize zeolite as support material it was necessary to perform a thermal treatment, which is composed by a pre-drying at 120°C and afterwards a calcination at 300°C under heating rate of $2^\circ\text{C}/\text{min}$ before treatment with methylaluminoxane (MAO) and bis(cyclopentadienyl) zirconium dichloride.

It was observed that high amounts of zirconium fixed on the support surface did not lead to catalysts with higher activities, but in general the molecular weights of the obtained polyethylenes were very high. Furthermore, the supported catalyst was submitted to a longer MAO pre-contact before starting the polymerization by feeding the monomer, causing a sharp increase in the catalyst activity.

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1. Introduction

In the field of polyolefins, the use of metallocene catalysts has allowed very rapid development [1]. The discovery of homogeneous catalytic systems comprising of metallocene and aluminoxane, opened a new era in the world of polyolefins [2]. Nevertheless, despite the great advantages gained by the advent of homogeneous metallocene catalysts for olefin homo- and co-polymerization, the former complexes, when compared with those of Ziegler–Natta conventional catalysts, have to be heterogenized to be used in

prevailing industrial processes, such as gas-phase and obtain uniform polymer particles with high bulk density [3], hopefully without the loss of catalytic activity stereo-chemical control, the ability to produce polymer with narrow molecular weight and chemical composition distribution and, when desired, long chain branches [4].

Kim and Choi reported that both the formation of catalytically active sites, like alkylation and formation of cationic species and the deactivation of these sites are very rapid processes. Generally a slow deactivation is observed in almost all polymerizations with metallocene/methylaluminoxane catalysts. A type of deactivation is attributed to the formation of inactive species with a Metal– CH_2 –Al structure [5]. Nevertheless, since the inactive species can be

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regenerated by methylaluminoxane (MAO), the polymerization decays slowly. Another deactivation that may occur is the bimetallic reaction, in which two Cp_2ZrCl_2 species interact, obtaining an inactive binuclear species [20]. In order to avoid these and other inherent problems, immobilization of the catalyst in a support has been preceded.

Metallocenes can be effectively supported on several inorganic oxides [7–18], the most commonly used are SiO_2 , MgCl_2 , Al_2O_3 , MgF_2 and CaF_2 [4]. The type of support as well as the technique used for supporting the metallocene and MAO has a crucial influence on the catalyst behavior [4]. Several techniques for immobilizing metallocenes and MAO have been proposed [4,7]:

- (1) adsorption of MAO onto the support followed by addition of the metallocene;
- (2) immobilization of the metallocene on the support, followed by contact with MAO in the polymerization reactor;
- (3) immobilization of the metallocene on the support, followed by treatment with MAO, producing a catalyst, which does not require MAO during polymerization, but generally requires aluminum alkyls.

The zeolite employed in this work was the acid ZSM-5 (H-ZSM-5) and as all zeolites, it is well known for their crystalline structure, defined narrow pore size distribution and large surface area [3]. According to some authors [3,9] zeolites are suitable supports because of the possibility of entrapping organometallic complexes in the pores.

Zeolites are crystalline aluminum-silicates, natural, silicon abundant, characterized by having a microporous structure, great internal superficial area compared to its external area. Its structure is composed by a tri-dimensional system where aluminum and silicon tetrahedrons are linked by the oxygen atoms. Aluminum and silicon atoms occupy the tetrahedron center, while the oxygen occupies the vertex. Due to the fact that oxygen atoms are shared by the center atoms, it makes the zeolite structure to have two times more oxygen than aluminum and silicon atoms. While aluminum is trivalent, there is a charge de-oscillation that must be equalized by other cations, called compensation cations [5].

There are many zeolite families, but the one studied in this work is the acid ZSM-5. They are natural zeo-

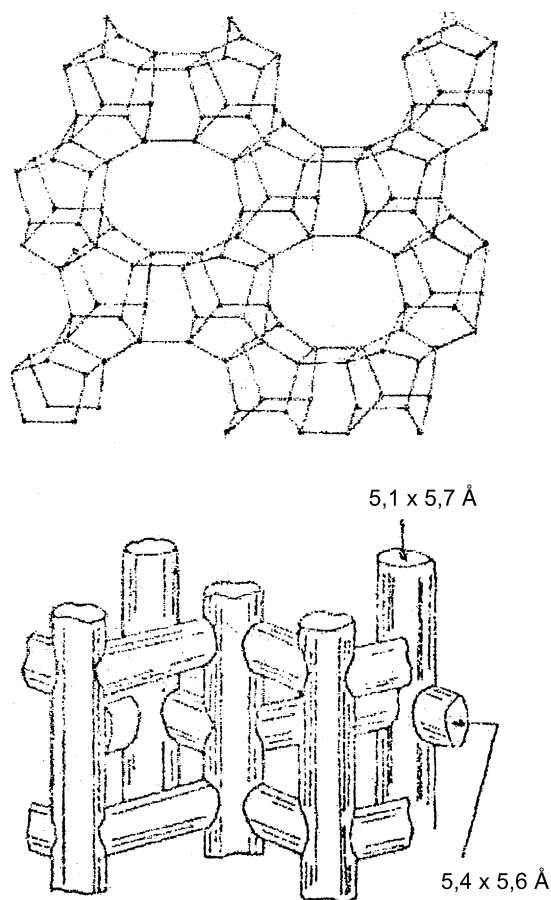


Fig. 1. Structure of H-ZSM-5 zeolite.

lites with Si/Al ratio >15 , which make these zeolites to have hydrophobic characteristics. Their channels are interconnected [19] as can be seen in Fig. 1. According to the previous works, a high Si/Al ratio on the zeolite structure favors the higher activity for the supported catalysts because of the stronger Lewis acidity of the Al sites [21]. Moreover, the compensation cation in the zeolite structure is supposed to be exchanged by the zirconocene cationic species.

To study the influence of some variables during the catalyst preparation on the system activity and polymer properties, supported catalysts were prepared varying the impregnation temperature of Cp_2ZrCl_2 ($\text{TCp}_2\text{ZrCl}_2$) and treatment concentration of MAO and Cp_2ZrCl_2 . Afterwards, the pre-contact time of the supported catalyst with MAO before starting the polymerization was examined.

Another important fact that was reported by Michellotti et al. is the de-alumination effect, which could partially create mesopores in the zeolite framework, and is supposed to be able to accommodate more easily the polymer growing chain at the active site [22].

2. Experimental

Zeolite H-ZSM-5 from PQ Corporation and CRI Zeolites Inc., CBU 8020, was used as support after a thermal treatment. The zeolite remained for 8 h at 120 °C. Afterwards, ca. 5 g was heated under nitrogen flow at heating rate of 2 °C/min, for 2 h at 300 °C.

Cp₂ZrCl₂ was used as received from Wako Pure Chemical Industry Ltd. MAO was donated by Witco as a 10% (w/w) toluene solution and was also used as received. Toluene was purified by refluxing and freshly distilled under nitrogen from a Na/benzophenone system. Nitrogen and polymerization-grade ethylene (from White Martins Brazil) were treated by passing through columns of Cu catalyst and activated molecular sieve (4 Å).

A mathematical experimental planning was performed with the variables of the supported catalyst preparation and the obtained data were treated using the program Statistica for Windows 4.3. Equation models were obtained relating the results to the independent variables. These models are considered valid in the studied ranges of investigation.

Three variables were studied: the impregnation temperature of Cp₂ZrCl₂ on the support, between 25 and 110 °C (X_1); the pre-treatment MAO concentrations varying from 0 up to 10 mmol Al/g (X_2); and Cp₂ZrCl₂ treatment concentrations varying from 0.05 up to 0.5 mmol Zr/g (X_3).

Operations were carried out under nitrogen using Schlenk techniques and two types of catalysts were prepared:

- (a) SO 1 series: The zeolite impregnation was carried out directly with Cp₂ZrCl₂ during 8 h. After impregnation the excess of Cp₂ZrCl₂ was thoroughly washed with toluene.
- (b) SO 2 series: The zeolite was pre-treated with MAO at room temperature for 12 h and then it was washed out with toluene at 90 °C prior to the impregnation with Cp₂ZrCl₂. The supported catalyst was thoroughly washed with toluene.

After its preparation polyethylene was synthesized using Cp₂ZrCl₂/MAO supported catalyst. All polymerization reactions were carried out in a 250 ml round-bottom glass flask equipped with a mechanical stirrer and gas inlet, at 50 °C for 1 h with pressure of 1.1 bar. The amount of the supported catalyst was maintained in 100 mg for each reaction. MAO concentration was 10 mmol for all the polymerizations.

Trying to optimize the performance of the supported catalysts on zeolite H-ZSM-5, the pre-contact time with MAO was examined.

In order to interrupt the reaction, acidified methanol was added. The polymer was filtered, washed with ethanol and dried at 60 °C.

The weight-average molecular weight (M_w) and molecular weight distribution (M_w/M_n) were determined by size-exclusion chromatography in 1,2,4-trichlorobenzene solution at 135 °C, using a Waters 150-CV-Plus gel-permeation chromatograph equipped with four Styragel HT columns, calibrated with standard polystyrenes.

Thermal properties of the polymers, such as melting temperature (T_m) and the crystallinity of the polyethylene were obtained using a differential scanning calorimeter measurement [6] in a Perkin-Elmer DSC-7 at heating rate of 10 °C/min.

3. Results and discussion

The obtained results of supported Cp₂ZrCl₂ catalyst on acid ZSM-5 in ethylene polymerization are expressed in Table 1.

The results show that the best polymerization yield was obtained when the zeolite was pre-treated with MAO and when a higher concentration of Cp₂ZrCl₂ was utilized.

The behavior of the prepared catalyst system was evaluated through the Statistica Program, using the normalized variables from -1 to +1, where x_1 is the impregnation temperature of Cp₂ZrCl₂ on the support, x_2 the MAO concentration, x_3 the Cp₂ZrCl₂ concentration and d is a constant.

3.1. Polymerization yield (Y_1)

The influence of the catalyst preparation conditions on the polymerization yield in the case

Table 1

Preparation of the supported catalyst and obtained results utilizing H-ZSM-5 as support material

Catalyst	TCp_2ZrCl_2 (°C)	[MAO] (mmol/g supplied)	$[Cp_2ZrCl_2]$ (mmol/g supplied)	Yield (g)	M_w/M_n	M_w (10^{-5})	T_m (°C)	Crystallinity (%)
1	70	5	0.275	2.51	2.2	8.5	135.5	52
2	70	5	0.275	1.96	n.d.	n.d.	134.2	37
3	25	0	0.050	0.60	n.d.	n.d.	134.7	39
4	25	0	0.500	0.64	n.d.	n.d.	135.0	41
5	25	10	0.050	0.57	n.d.	n.d.	135.0	41
6	25	10	0.500	5.72	4.1	3.9	133.6	59
7	110	0	0.050	0.22	n.d.	n.d.	133.7	19
8	110	0	0.500	0.62	n.d.	n.d.	133.8	61
9	110	10	0.050	1.68	n.d.	n.d.	135.0	58
10	110	10	0.500	0.87	n.d.	n.d.	134.7	50

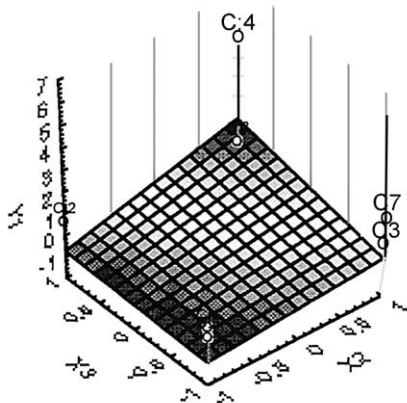
Polymerization conditions: 100 ml toluene; 100 ± 10 mg of supported catalyst; [MAO] = 10 mmol; bath temperature, 50 °C; ethylene pressure, 1.1 bar; polymerization time, 1 h.

of H-ZSM-5 support was represented by the Eq. (1).

$$Y_1 = a_1x_1 + a_2x_2 + a_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + c_{123}x_1x_2x_3 + d \quad (1)$$

where $a_1 = -0.517$; $a_2 = 0.845$; $a_3 = 0.597$; $b_{12} = -0.417$; $b_{13} = -0.700$; $b_{23} = 0.487$; $c_{123} = -0.790$; $d = 1.365$.

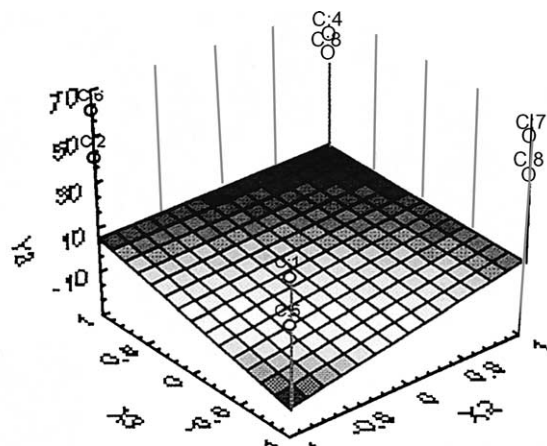
The correlation coefficient is 1.000.



Y_1 = Polymerization yield
 X_2 = [MAO] (normalized variables: -1 to +1)
 X_3 = $[Cp_2ZrCl_2]$ (normalized variables: -1 to +1)

Fig. 2. The parameters that most influenced the ethylene polymerization yield (Cp_2ZrCl_2 supported on ZSM-5/MAO).

The greater influence on the polymerization yield was given by metallocene and MAO concentrations. The enhancement of these variables improved the polymerization yield once the zeolite is used, the ZSM-5 has many Brönsted acid sites and, therefore, the zeolite pre-treatment is necessary in order to neutralize these deactivating sites. In this way, the fixation of MAO over these Brönsted acid sites provides the impregnation sites for the metallocene catalysts.



Y_3 = Crystallinity
 X_2 = [MAO] (normalized variables: -1 to +1)
 X_3 = $[Cp_2ZrCl_2]$ (normalized variables: -1 to +1)

Fig. 3. The parameters that most influenced the crystallinity of polyethylene obtained by Cp_2ZrCl_2 supported on ZSM-5/MAO.

Table 2
Catalyst characterization

Catalyst	TCp_2ZrCl (°C)	[MAO] (mmol/g supplied)	$[Cp_2ZrCl_2]$ (mmol/g supplied)	Zr fixed $\times 10^3/g$ Zr fixed $\times 10^3/g$	Activity (g of PE/g of catalyst)	Activity (kg of PE/mol Zr \times h)
1	70	5	0.275	24.1	25.1	104.1
2	70	5	0.275	21.9	19.6	89.4
3	25	0	0.050	14.2	6.0	42.1
4	25	0	0.500	16.4	6.4	38.9
5	25	10	0.050	9.9	5.7	57.8
6	25	10	0.500	14.2	57.2	401.4
7	110	0	0.050	36.2	2.2	6.1
8	110	0	0.500	104.1	6.2	5.9
9	110	10	0.050	41.7	16.8	40.3
10	110	10	0.500	32.9	8.7	26.4

On the other hand, the increase of the impregnation temperature of Cp_2ZrCl_2 on the support caused a decrease in the catalyst activity, suggesting that the catalyst deactivation reaction during the support treatment was increased.

In order to visualize the parameters that most influenced the polymerization yield, the graphic as shown in Fig. 2 was constructed.

3.2. Melting Temperature— T_m (Y_2)

The result of the statistic treatment for the influence of catalyst preparation conditions on T_m of polyethylene can be represented by Eq. (2).

$$Y_2 = a_1x_1 + a_2x_2 + a_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + c_{123}x_1x_2x_3 + d \quad (2)$$

where $a_1 = -0.137$; $a_2 = 0.137$; $a_3 = -0.162$; $b_{12} = 0.412$; $b_{13} = 0.112$; $b_{23} = -0.262$; $c_{123} = 0.162$; $d = 134.437$.

The correlation coefficient is 1.000.

Only the MAO concentration influenced significantly the melting temperature of polyethylene. This means that the presence of MAO on the support surface led to more stabilized active sites after Cp_2ZrCl_2 immobilization, which provides more linear polymer chains and, therefore, more perfect polymer crystals.

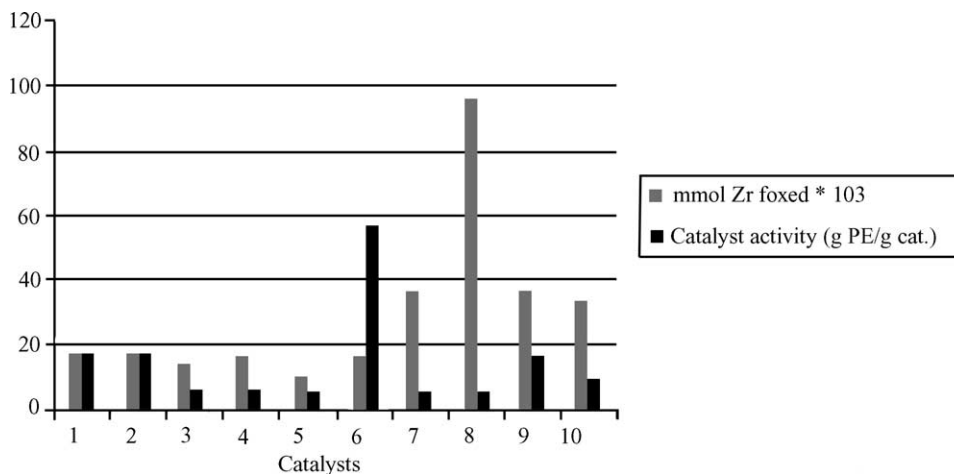


Fig. 4. Catalyst activity (Cp_2ZrCl_2 supported on ZSM-5/MAO) on ethylene polymerization and Zr content on support surface.

3.3. Crystallinity (Y_3)

Its behavior was better represented by the model described through Eq. (3).

$$Y_3 = a_1x_1 + a_2x_2 + a_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + c_{123}x_1x_2x_3 + d \quad (3)$$

where $a_1 = 0.937$; $a_2 = 5.912$; $a_3 = 6.737$; $b_{12} = 1.087$; $b_{13} = 1.812$; $b_{23} = -4.412$; $c_{123} = -8.237$; $d = 45.962$.

The correlation coefficient between the predicted and the obtained values is equal to 1.000, which shows a good relation between the parameters.

The enhancement of MAO and CP_2ZrCl_2 concentrations improved the crystallinity of the obtained polyethylene. This was probably because the zeolite H-ZSM-5, as already mentioned, has many Brönsted acid sites and MAO pre-treatment is fundamental in order to have an efficient fixation of the metallocene, leading to more stable active sites, with less chain transfer reaction.

Through the graphic as shown in Fig. 3, the greater influence on polymer crystallinity can be demonstrated.

Due to the impossibility of obtaining the values of molecular weight and molecular weight distribu-

tion for all the obtained polyethylene by using the gel-permeation chromatograph, once some product was not soluble in the analysis conditions, it is assumed that the molecular weights of these polymers are extremely high. Therefore, the analysis of their behavior using the statistic program was not practicable to be done.

The contents of zirconium and aluminium on the support were measured by an inductively coupled plasma spectrophotometer (ICP-AES). The results are as shown in Table 2.

From the results it is possible to observe that higher activity does not mean larger content of zirconium fixed on the support. This fact can be illustrated in Figs. 4 and 5.

It is suggested that some bimetallic de-activation occurs during the immobilization procedure, especially at higher temperatures and higher zirconocene concentrations.

From Fig. 6, it is possible to observe the conditions that promote a better fixation of the catalyst. As already written, a great content of zirconium fixed on the support surface does not mean a good catalyst activity.

Utilizing the preparation conditions that led to the best polyethylene productivity, the pre-contact time between the heterogeneous catalyst and MAO

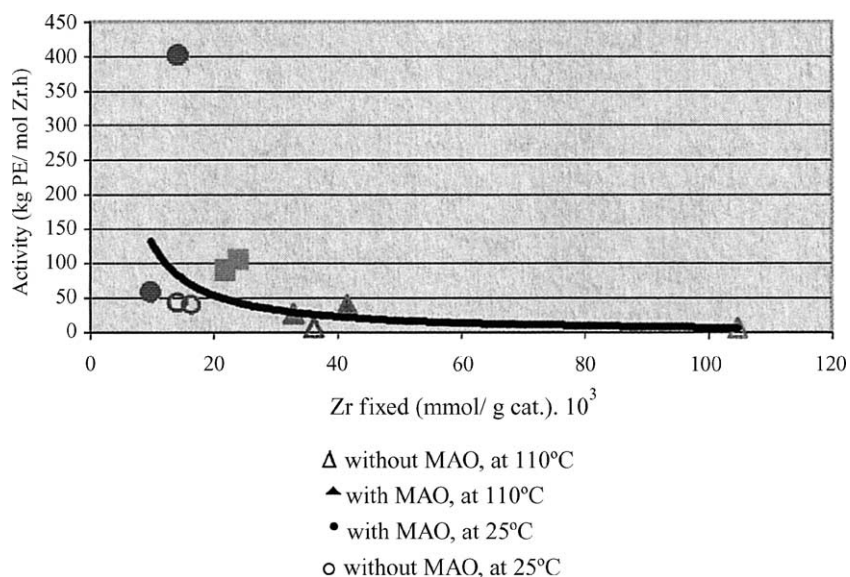


Fig. 5. The preparation conditions of the supported catalysts and its relationship between catalyst activity and Zr content.

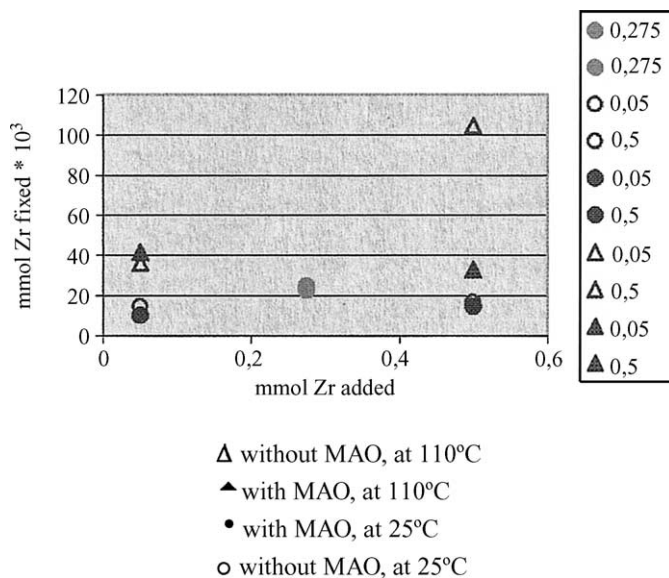


Fig. 6. Zr amount fixed used on the supported catalysts (Cp_2ZrCl_2 on ZSM-5/MAO).

solution was increased for 3 h and the results are expressed in Table 3.

The increase of pre-contact time promoted a sharp increase in the polymerization yield. This is due to the fact that the alkylation of the catalytic complex was promoted by the longer pre-contact time, generating a greater number of active sites since the beginning of the polymerization. On the other hand, by the increase of the pre-contact time, the molecular weight of the obtained polyethylene decreased, and the molecular weight distribution was broadened. This shows that significantly more chain transference reactions had occurred. At the same time, the melting temperature of the produced polyethylene was decreased, which indicates the presence of chain branching, probably due to

the incorporation of insaturated macro-monomer derived from the chain transfer reactions.

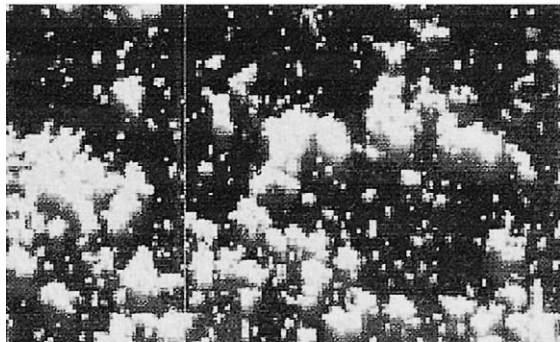
The differences of polymer morphology were observed with the increase of pre-contact time as shown in Fig. 7, together with the polyethylene produced by the homogeneous catalyst. Fig. 7(b) shows that the supported ZSM-5 catalyst was able to control appropriately the polymer morphology, without fine particles derived from the homogeneous catalyst system, as shown in Fig. 7(a). It can be observed in Fig. 7(c) that some fine particles have arisen from the polymerization at longer pre-contact time. This shows that MAO had extracted some active sites from the catalyst surface, which generated some homogeneous catalysis.

Table 3
Obtained results for the pre-contact time variation

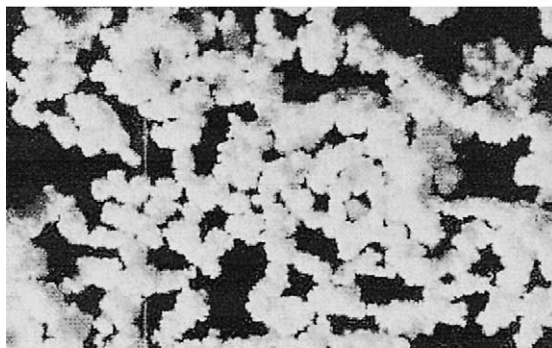
Catalyst	Pre-contact time (mm)	Yield (g)	M_w/M_n	$M_w \times 10^{-5}$ (g/mol)	T_m ($^\circ\text{C}$)	Crystallinity (%)	Activity (g of PE/g of catalyst)	Activity (kg of PE/mol of Zr \times h)
7	5	5.72	4.1	3.9	133.6	59	57.2	402.8
7	180	15.31	4.8	2.4	130.9	59.1	153.1	1078.2
Homogeneous	5	10.90	2.0	1.46	131	65	109.0	2180

Polymerization conditions: 100 ml toluene; 100 ± 10 mg of supported catalyst; $[\text{MAO}] = 10$ mmol; bath temperature, 50°C ; ethylene pressure, 1.1 bar; polymerization time, 1 h.

a: Homogeneous polymerization (30X)



b: Heterogeneous polymerization – 5 min of precontact time (30X)



c: Heterogeneous polymerization – 180 min of precontact time (30X)



Fig. 7. Differences of morphology of polyethylene produced with homogeneous and supported catalyst on H-ZSM-5 zeolite: (a) homogeneous polymerization (30X); (b) heterogeneous polymerization, 5 min of pre-contact time (30X); (c) heterogeneous polymerization, 180 min of pre-contact time (30X).

4. Conclusions

Higher content of metallocene fixed on the support surface had occurred at higher impregnation temperature, without MAO in the pre-treatment of the support and with high amounts of zirconium. Nevertheless, higher activity was obtained when the catalyst was fixed at lower temperatures, with MAO pre-treatment and with high amounts of zirconocene. In summary, while utilizing high temperatures of metallocene impregnation, bimetallic deactivation enhanced, causing a decrease in the catalyst activity. Another important aspect in case of this zeolite is that MAO pre-treatment is necessary due to the presence of Brønsted sites on the zeolite structure.

The great contribution of this research was to observe that the increase of pre-contact time of the supported catalyst with MAO promoted a sharp enhancement of the polymerization yield, since alkylation was more effective, generating a great number of effective active sites. On the other hand, this MAO pre-contact time promoted some leaching of the active sites, which produced the formation of a low content of fine polymer particles.

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