

Polyethylene Synthesis Catalyzed by Cp_2ZrCl_2 Supported on Mordenites with Different Physico-Chemical Properties

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The commercial zeolite sodic mordenite was chemically and thermally treated in order to obtain materials with different physico-chemical properties to be employed as support for the metallocene bis(cyclopentadienyl)zirconium dichloride used for ethylene polymerization. The supports obtained were characterized regarding their chemical composition, textural properties as well as Lewis and Brønsted sites concentrations. It was verified that the original zeolite without dealumination treatment was the most active catalyst followed by the material dealuminated with steam. All the supported catalysts produced polyethylene with higher molecular weight in relation to that obtained with the homogeneous counterpart.

Key words: Polyethylene (PE), Zeolites, Metallocene Catalysts

Introduction

Although the homogeneous metallocene systems offer significant advantages for the commercial use, several disadvantages have to be overcome, such as the low molecular weight of the produced polymers, low stability of the catalysts at high temperatures and the reactor fouling, which demand successive interruptions for cleaning. Many authors studied the heterogenization of metallocene complexes on different supports [1–5] in order to prepare polymerization catalysts with activities as high as the homogeneous systems. This process would also allow the substitution of the technology used with the conventional Ziegler-Natta catalysts in current plants, favoring the technology of metallocene catalysts.

Different authors have reported the use of zeolites as support [6–8] for metallocene compounds. A variety of zeolites Y and sodic mordenite (NaM) were evaluated as supports for bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2) in ethylene polymerization. Contrary to our initial expectation, the most active catalyst was the one supported on mordenite, which has a smaller specific surface area than the Y zeolite. The results indicate that the concentration of Al species (expressed by the Si/Al ratio – SAR) on the support crystalline framework is the dominant parameter for

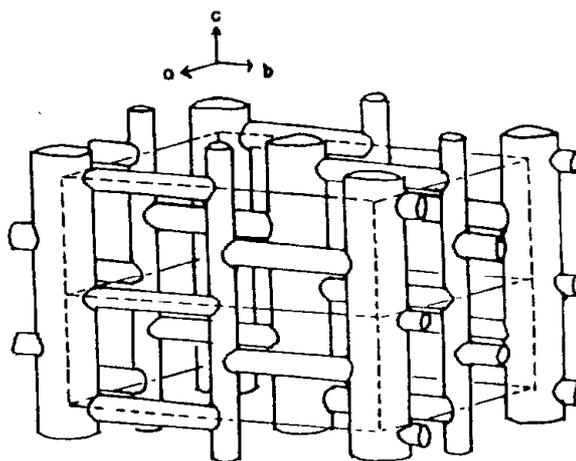


Fig. 1. Mordenite porous structure [11].

producing highly active catalyst, although the external surface is certainly also an important factor [9, 10].

Mordenite is a large pore zeolite having a porous structure formed by two types of elliptical channels, as shown in Fig. 1. The main channels are formed by rings of 12 atoms of oxygen, with size apertures of $7.1 \times 6.7 \text{ \AA}$. The secondary ones, parallel to the plane formed by the axes *c* and *b*, are constituted by rings of 8 oxygen atoms, with apertures [11] of $5.7 \times 2.9 \text{ \AA}$. These secondary channels are inaccessible for most

of the organic molecules and do not allow an effective communication among the main channels. For this reason, mordenite porous systems are considered as pseudo-one-dimensional. Dealumination is generally meant to reduce these characteristics by generating a mesoporous system and by reducing the acid site density.

Catalysts with similar transition metal contents on the same support may have activities varying considerably, depending on the conditions of the preparation of the supported catalysts such as the metallocene immobilization temperature and the support treatment.

In a previous work using zeolite NaM as support, the conditions to prepare highly active catalysts which produce polyethylene with high molecular weight and melting temperature were shown to be impregnation temperatures from 30 to 110 °C, low catalyst concentrations with no pretreatment of mordenite with methylaluminoxane (MAO), as applied in the case of silica supports [12].

The need for chemical pretreatment of a support depends on the type of active groups on its surface. For NaM, the pretreatment with MAO solution is not recommended, since there is a relatively low amount of silanol groups on its surface for MAO to react and to be fixed [9, 10]. On the other hand, upon employing the zeolite H-ZSM-5 for the immobilization [13] of Cp_2ZrCl_2 , it was observed that the most active catalysts were obtained with the support pretreated with MAO solution.

Michelloti *et al.* [14] have also studied the system Cp_2ZrCl_2 supported on HY employing different preparative methods. According to the authors, the catalyst activity of the supported systems was much lower than that with the homogeneous precursor, although the pretreatment with methylaluminoxane (MAO) or trimethylaluminum (TMA) solutions have both enhanced the activity. In this study it was also shown that the molecular weight of the polymers produced with the zeolite-supported catalysts are higher than those obtained with the homogeneous counterpart. This is due to the stabilization of the cationic metallocene species and the difficulty imposed on the β -agostic interaction, which promotes the hydrogen transfer chain reactions of the growing polymer chain to the transition metal in the catalyst active site. An increase in the polymerization temperature led to an increase in the catalyst productivity but the molecular weights have sharply decreased. Moreover, the factor that most influenced the activity of the zeolite-supported catalyst was

the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the crystalline framework; the decrease of this parameter from 27 down to 5.7 is accompanied by a sharp decrease of the catalyst activity. It was suggested that the dealumination process creates mesopores in the zeolite structure, which are capable to more easily accommodate the growing polymer chain in the active center.

The objective of the present work was to evaluate a series of dealuminated mordenites obtained through acid and/or hydrothermal treatment, in order to obtain samples with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios (SAR) and also different amounts of extra-framework aluminum species (EFAL), developed as support for metallocene catalysts.

Results and Discussion

The X-ray diffractograms of the parent mordenite and the modified samples are presented in Fig. 2. For all samples, the diagrams show narrow lines, which indicate that the treatments did not affect the crystalline structure of the zeolite.

The results of characterization by atomic absorption spectrometry and by ^{29}Si and ^{27}Al NMR spectroscopy are presented in Table 1.

^{27}Al MAS/NMR analysis showed that the parent mordenite (NaM) had no octahedrally coordinated aluminum atoms, *i.e.*, no extra-framework aluminum species was detected. The framework Si/Al ratio obtained by ^{29}Si MAS/NMR was slightly lower than that obtained by global Si/Al (AAS), indicating that this sample contained silanol groups (SiOH), which are associated with structural defects and are dangling OH's at crystal boundaries [11].

The acid leaching of the ion-exchanged mordenite (HM) significantly removed the framework aluminum,

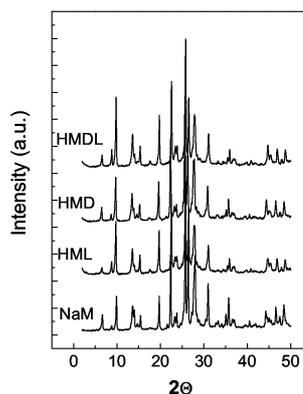


Fig. 2. X-ray powder diffractograms of the mordenites used as supports.

Table 1. Chemical composition of the supports.

Support	Na/Al*		Si/Al (molar)	
	(molar)	AAS global	^{29}Si NMR	^{27}Al NMR
NaM	1.0	5.7	4.8	5.7
HMD	0.5	5.9	8.2	8.0
HML	0.1	13.3	12.3	19.3
HMDL	0.1	25.7	12.8	37.0

* AAS.

as shown by the increase in both global and framework Si/Al ratios. The defects associated with silanol groups were also increased, as indicated by the Si/Al ratios obtained by ^{29}Si MAS/NMR, which are lower than those obtained by ^{27}Al MAS/NMR and AAS. The presence of a peak associated with octahedrally coordinated aluminum atoms in the ^{27}Al MAS/NMR spectrum ($\delta = 0$ ppm) indicates that part of the aluminum to be extracted from the framework was retained inside the porous structure as extra-framework aluminum. The presence of these extra-framework aluminum species explains the higher Si/Al ratios obtained by ^{27}Al MAS/NMR in comparison to those obtained by the global ratio.

Comparing the Si/Al ratios of samples HML and HMD, one can conclude that steaming at 550 °C removes less framework aluminum than the acid leaching. Due to the specific characteristics of steaming, all extra-framework aluminum species formed were retained inside the pores, as confirmed by similar Si/Al global ratios of samples NaM and HMD. Silanol groups were also present in the steamed samples (HMD). This may be a consequence of the short duration of the hydrothermal treatment, which prevented complete silicon reinsertion into the hydroxyl nests, as also observed by Fernandes *et al.* [15]. Subsequent acid leaching, producing the HMDL sample, apparently did not remove the extra-framework aluminum species formed in the steaming, although it has significantly dealuminated the framework structure, forming additional defects.

Table 2 presents the main textural characteristics of the parent mordenite along with those of the dealuminated samples.

The parent mordenite, NaM, had a microporous volume lower than the theoretical value for a well-synthesized mordenite [15] (about 0.22 cm³/g), indicating the presence of residual material from the synthesis, which partially blocks the pores of the zeolite. After ion exchange with HCl, an increase in both area and pore volumes was observed (sample HM), indicating that part of this residual material was removed.

Table 2. Textural characteristics of the zeolites.

	NaM	HM	HMD	HML	HMDL
S_{BET} [m ² /g]	344	394	338	465	486
$S_{external}^a$ [m ² /g]	13	17	9	28	43
$V_{micropore}^a$ [cm ³ /g]	0.154	0.183	0.161	0.218	0.222
$V_{mesopore}^b$ [cm ³ /g]	0.018	0.036	0.014	0.033	0.046

^a t-plot; ^b BJH method – 20–600 Å.

The acid leaching of the HM sample apparently completes this removal, since the theoretical value for the microporous volume of mordenites was reached for the HML sample. NMR analyses showed the presence of EFAL on this sample, so it can be speculated that extra-framework aluminum species are located inside the mesopores produced during the framework aluminum extraction.

The decrease in area and pore volume for the HMD sample, when compared with HM, can be associated with the significant presence of extra-framework aluminum atoms blocking the pores. When this sample was acid-leached, forming an HMDL sample, part of this extra-framework aluminum was indeed removed, causing an increase in both pore volumes (micro- and mesopores) and specific areas. This increase is indicative of the incipient formation of mesopores, which are partially blocked by the extra-framework aluminum species still present in this sample.

Fig. 3 shows the FTIR spectra of pyridine adsorbed on the dealuminated zeolites used as supports. After pyridine adsorption/desorption at 200 °C, the presence of bands at 1542 cm⁻¹, corresponding to Brønsted acid sites, and at 1455 cm⁻¹, corresponding to Lewis sites and also at 1489 cm⁻¹, corresponding to the adsorption in both type of sites, were observed. For the HMD sample, a band at 1445 cm⁻¹, associated with the interaction between pyridine and Na⁺ cations was observed.

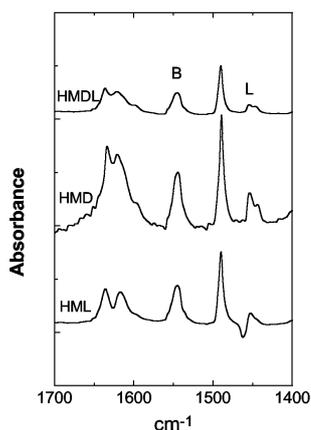


Fig. 3. FTIR spectra of pyridine adsorbed on the dealuminated zeolite.

Table 3. Brønsted and Lewis acid sites concentration (mmol/gcat) of the supports.

Support	L	B	L/B
HMD	4.85	12.80	0.38
HML	3.56	8.10	0.44
HMDL	1.04	4.12	0.25

Table 4. Results of Zr analysis on the zeolite-catalysis of ethylene polymerization.

Catalyst	Zr fixed [w/w%]	Yield [g]	Activity [kgPE/molZr h]
Cp_2ZrCl_2	–	10.91	2180
$\text{Cp}_2\text{ZrCl}_2/\text{NaM}$	0.22	6.40	2676
$\text{Cp}_2\text{ZrCl}_2/\text{HMD}$	0.32	4.22	1208
$\text{Cp}_2\text{ZrCl}_2/\text{HML}$	0.21	0.72	315
$\text{Cp}_2\text{ZrCl}_2/\text{HMDL}$	0.12	0.26	199

Conditions: 100 ml of toluene, [MAO] = 0.1; 100 mg of supported catalyst; 1.1 atm of monomer; homogeneous catalyst: $[\text{Zr}] = 50 \mu\text{M}$.

Mokaya and Jones [16] attributed bands at 1445 and 1594 cm^{-1} to pyridine weakly associated with hydrogen atoms of the silanol groups. Other bands were observed at 1630 cm^{-1} , associated with pyridinium ions formed at Brønsted acid sites, and at 1620 cm^{-1} , also related to Lewis acid sites.

Table 3 presents the concentration of Brønsted (1542 cm^{-1}) and Lewis (1455 cm^{-1}) acid sites for the dealuminated samples. The values are expressed in mmols of pyridine/gram of zeolite and were calculated from integrated absorbances. Molar absorptivities employed were those calculated by Emeis [17] ($\epsilon\text{B} = 1.67 \text{ cm}^2/\text{mmol}$ and $\epsilon\text{L} = 2.22 \text{ cm}^2/\text{mmol}$).

Table 4 shows the fixed zirconium content on the prepared catalysts from ICP analysis and the results obtained in ethylene polymerization with the bis(cyclopentadienyl)zirconium dichloride catalyst systems.

It can be observed that despite the same conditions of the catalysts preparation, the amount of Zr fixed on the supports and the catalyst activities varied significantly.

The HML support has fixed the same amount of Zr as the original NaM, and yet there is a sharp decrease in catalyst activity. This support, obtained by treatment of NaM with hydrochloric acid, has improved textural properties, such as higher surface and external areas, as well as higher micro- and mesopore volumes. As mentioned earlier, the acid treatment probably removes some extra-framework aluminum species from the zeolite pores. The SAR value of the HML support is much higher than that of NaM or HMD supports, although the amounts of Lewis and Brønsted sites on its

Table 5. Ethylene properties obtained with the supported catalysts.

Catalyst	T_m [°C]	X_c [%]	$M_w \times 10^{-3}$ [g/mol]	M_w/M_n
Cp_2ZrCl_2	131	65	146	2.0
$\text{Cp}_2\text{ZrCl}_2/\text{NaM}$	134	40	471	2.3
$\text{Cp}_2\text{ZrCl}_2/\text{HMD}$	134	43	504	2.2
$\text{Cp}_2\text{ZrCl}_2/\text{HML}$	134	42	486	2.1
$\text{Cp}_2\text{ZrCl}_2/\text{HMDL}$	134	43	502	2.2

surface are lower and the amounts of silanol group has increased extensively.

On the other hand, the catalyst supported on HMD has fixed higher amounts of Zr and its activity is higher than that of the catalyst $\text{Cp}_2\text{ZrCl}_2/\text{HML}$, but lower than that of the catalyst supported on NaM. Although extra-framework aluminum species has not been removed from HMD pores and the support has a higher silanol contents in comparison with NaM, the amounts of Lewis and Brønsted acids sites are the highest among all supports, also with a high L/B ratio. This may explain the highest activity of the HMD supported catalyst in comparison with the HML supported one, where the Lewis acid sites fix zirconium in a potentially active form rather than the Brønsted acid sites, which fix zirconium in a non-active form.

The HMDL support, which was obtained by further acid treatment of the HMD zeolite, gave the lowest Zr amount and a less active catalyst. These results can be related both to the low amounts of Lewis and Brønsted acid species left on the support surface and to the low proportion of L/B types of sites, which could be sites for fixation of zirconium species, either in potentially active or non-active forms.

Regarding the properties of the obtained polyethylene (Table 5), significant variations in the molecular weights and the crystallinity degree were found only between the polymers obtained from the homogeneous system and those obtained from the supported ones. As expected, all polyethylene produced with the supported catalysts presented superior molecular weights compared to that obtained with the homogeneous system and, consequently, those polymers have a lower degree of crystallinity. The polydispersion was narrow for both the homogeneous as well as the supported catalysts.

Conclusions

This study has shown that treatment of zeolite NaM with hydrochloric acid or with steam and hydrochloric

ric acid strongly dealuminates the zeolite framework, enhancing the surface and external areas as well as the pore volumes. However, these materials after loading with Cp_2ZrCl_2 result in supported catalysts with lower activities for ethylene polymerization. On the other hand, the support obtained by thermal treatment gave better catalyst activity.

Experimental Section

Chemicals

Ethylene and nitrogen were purified by molecular sieves and copper catalyst columns. MAO was kindly donated by Crompton, Germany, as a 10% toluene solution and used as received. Toluene was distilled from the sodium benzophenone complex. Cp_2ZrCl_2 from Wako Pure Chemical Ind. Ltd. was used as received.

Preparation of supports

A commercial Na-mordenite (CP-500-11, from PQ Corporation) with SAR = 11.4 (AAS) was the parent material and was also tested as support (NaM). It was ion-exchanged with 0.5 mol/L hydrochloric acid solution (250 ml/25 g zeolite) in a filter at room temperature. Afterwards, it was repeatedly washed with distilled water to achieve complete chloride elimination, and then dried at 110 °C overnight. The modified sample (HM) was submitted to three different treatments aiming to obtain mordenites with different textural and acid properties to be tested as supports for zirconocene catalysts. In the first treatment, HM was acid leached with a 4M hydrochloric acid solution under reflux for 2 h with a ratio of acid volume/zeolite weight equal to 30. This sample was named HML. The second procedure corresponded to a hydrothermal treatment at 550 °C for 2 h to form samples HMD. Part of this sample was further leached under the same conditions, producing the HMDL sample.

Characterization of the supports

The chemical composition of the samples was determined by flame atomic absorption spectrometry (FAAS) using a Perkin Elmer 1100B spectrometer. The framework silica to alumina ratio (SAR) and the presence of extra-framework aluminum species were determined by solid-state ^{29}Si and ^{27}Al MAS/NMR, in a Varian VRX-300 FT-NMR spectrometer [9]. X-ray powder diffraction (XRD) was performed using a Miniflex/Rigaku diffractometer, with monochromated $\text{Cu-K}\alpha$ radiation.

Textural properties were determined by nitrogen adsorption at -196 °C in a Micromeritics ASAP 2000. Prior to these measurements, the samples were treated under vacuum at 573 K for 3 h. FTIR measurements were carried

out using pyridine as the probe molecule. The zeolite samples were pressed into self-supported wafers (9.8 mg/cm²) and activated in the IR cell under O_2 and in a vacuum at 450 °C for 3 h. A Perkin Elmer FTIR spectrometer model 2000 was used. Pyridine was adsorbed at 150 °C and after outgassing at the same temperature, the concentration of Brønsted and Lewis sites able to retain pyridine at 150 °C was determined using the integrated bands absorbance at 1545 and 1450 cm^{-1} , respectively, being absorptivities determined by Emeis [17].

Preparation and characterization of catalysts

Before incorporation of the active phase, the mordenites used as supports were reactivated by heating under N_2 at 2 °C/min up to 300 °C, keeping them at this temperature for 2 h, cooling down to room temperature and storing under N_2 . All operations involved in catalyst preparation were performed under nitrogen using Schlenk techniques. 1 g of the activated support was treated at room temperature for 8 h with a solution containing 0.05 mmol of Cp_2ZrCl_2 in toluene. The solid was then washed with toluene and dried under high vacuum. The fixed zirconium content on the catalysts was measured using a X-Ray fluorescence spectrophotometer Rigaku, model B3 with a Geigerflex generator and a molybdenum anode (LiF crystal analyzer, NaI detector). The analysis was performed measuring the analytical line of $\text{Zr-K}\alpha$ (1) in comparison to a calibration curve.

Ethylene polymerization

All ethylene polymerizations were carried out in a 250 ml reactor filled with 100 ml of toluene and 5.8 ml of methylaluminumoxane solution at 1.1 bar of ethylene. A suspension of 100 mg of supported catalyst was added in the reactor under ethylene flow at 50 °C. Ethylene pressure was maintained constant by continuously feeding during the polymerization. After 1 h of polymerization, ethylene was purged and ethanol (5% HCl) was added. The polymer was washed with ethanol and water and dried in a vacuum oven at 60 °C.

Polymer characterization

The obtained polymers were characterized by melt temperature (T_m), crystallinity (x_c), weight-average molecular weight (M_w) and polydispersity (M_w/M_n). Differential Scanning Calorimetric Analysis (DSC) was carried out between 50 °C and 250 °C using a heating rate of 10 °C/min in a Perkin-Elmer DSC-7. The crystallinity was calculated by the enthalpy value obtained in the second heating period and the theoretical value for 100% crystalline polyethylene (293 J/g). Gel Permeation Chromatography Analysis (GPC) was performed at 135 °C, with dichlorobenzene as the solvent and HT6E, HT3, HT4 μ -Styragel columns (Waters), calibrated with standard monodisperse polystyrenes.

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