Research Article

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Preparation of polypropylene-based nanocomposites using nanosized MCM-41 as support and *in situ* polymerization

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Abstract

MCM-41 nanoparticles were used for preparing nanocomposites through the *in situ* polymerization of propylene. The performance of the catalytic system and the final properties of the materials obtained are highly dependent on the methodology used for impregnation of the catalyst onto the support particles, and therefore an optimization study for the impregnation methodology of the catalyst ($Me_2Si(Ind)_2ZrCl_2$) was carried out. Two different methodologies were used; the results in terms of catalytic activity and polymer molecular masses indicated that the most promising one involved the pre-activation of the catalyst with the cocatalyst, methylaluminoxane, followed by impregnation onto the MCM-41 nanoparticles. Thus, an optimized route for the preparation of polypropylene nanocomposites achieving significant improvements in catalyst activity was developed. The nanocomposite materials were characterized by GPC, TGA and DSC. The dispersion state and the size of the nanoparticles incorporated in the polypropylene matrix were investigated by transmission electron microcopy. Additionally, this methodology allows simultaneous control of the desired amount of support and the concentration of catalyst to be used in the *in situ* polymerization.
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Keywords: MCM-41 nanoparticles; supported catalyst; metallocene catalyst; polypropylene; nanocomposites

INTRODUCTION

In recent years, thanks to intense scientific research, polypropylene (PP) has greatly evolved due to the inclusion of this polymer in the development of new materials, e.g. those called composites. Composites are obtained by the inclusion of different substances known as fillers dispersed in the matrix in order to improve or add new properties to the polymers for more specific and new technological applications.

More recently the use of fillers of nanometric dimensions has generated a new range of materials known as nanocomposites. These fillers are incorporated into the polymer by methods such as mechanical mixing in the molten state[1,2] and also by *in situ* polymerization.[3-6] This last route involves the incorporation of the particles during the polymerization process. It is shown that this offers advantages such as good dispersion of the particles in the polymer plus some significant changes in properties of the final product.[7]

On the other hand, with respect to the synthesis of PP, today the development of catalysts has enabled polymers to be obtained in which structural control has reached very high levels. Metallocene catalysts with high catalytic activity are included in this area, allowing highly stereoregular PP to be obtained.[8]

With respect to catalytic studies, great emphasis continues in supported-catalysis-related research concerning the implementation of new supports and impregnation techniques. The most commonly used substrates are silica based materials, which include the family of mesoporous silicas such as MCM-41 and SBA-15, among others. These have been used as support systems for zirconocenes

for polyethylene synthesis with different impregnation techniques giving interesting results in the morphology of the polymers and leading to the incorporation of these substances into the polymer matrix.[9-13]

Also catalytic systems based on zirconocene have been implemented for the polymerization of propylene *in situ* by impregnation on commercial silica using different impregnation techniques. Some results show increase in the molecular weight of the polymer.[14]

With respect to impregnation techniques, some studies show that the amount of the catalyst that can be impregnated increases and provides better catalytic activity in polymerization by

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pretreating the support with methylaluminoxane (MAO).[15,16] However, exceptions to this behavior may be found in the case of Ga-MCM-41 supports and also for purely siliceous MCM-41 if excess MAO coverage is use.[17,18] These studies indicate that the MAO to be used both in the pretreatment and in the polymerization reaction is a critical parameter, which must always be studied to optimize the catalyst system preparation.

The development of supported catalysts for polymerization has evolved with the implementation of nanosized and nanostructured supports. These have shown improvements with respect to catalytic activity compared to those with sizes on the micrometer scale.[19] Recently the synthesis of mesoporous silicas has allowed MCM-41 nanoparticles to be obtained. Their high surface area, large pore size and nanometric particle size enable these materials to immobilize well-dispersed catalyst molecules with reduced constraints to mass transfer.[20] Therefore, these materials are good candidates to be used as supports and further incorporated in the polymer matrix, thus opening up the possibility of studying the final product as a nanocomposite.

In this paper we propose to obtain nanocomposites of PP using MCM-41 nanoparticles (NMCM-41). The NMCM-41 can simultaneously act as filler and support for the $Me_2Si(ind)_2ZrCl_2$/MAO catalytic system. In a first step the optimization of the impregnation procedure and the effects on catalytic activity and molecular weight are discussed. Subsequently NMCM-41 based nanocomposites are prepared by *in situ* polymerization using a novel and straightforward impregnation methodology. This greatly simplifies the preparation of the supported catalyst and allows the desired amounts of filler, the catalyst load on NMCM-41 and the catalyst concentration in the reaction medium to be controlled.

EXPERIMENTAL

Materials and reagents
All manipulations were performed in a dry chamber under an inert atmosphere of extra pure dry nitrogen by using the Schlenk technique. Nanoparticles of MCM-41 were prepared according to the procedure described elsewhere.[19] Toluene is distilled in the presence of metallic sodium and benzophenone (were all obtained from Aldrich, Germany). MAO 10 wt% in toluene and the catalyst *rac*-$Me_2Si(Ind)_2ZrCl_2$ from Chemtura, Germany, were used as received.

Catalyst impregnation
Method A
The MCM-41 nanoparticles were dried at 400 °C under nitrogen stream and vacuum rounds. Subsequently, 0.5 g of these was placed in contact with 1.5 mmol of MAO in a toluene suspension with stirring for 16 h. Then the solid was washed with toluene to remove excess MAO and allowed to dry under a nitrogen stream. The dried particles were suspended again in dry toluene and contacted with the metallocene catalyst (0.7 wt% Zr) under stirring for 16 h. Subsequently, the process of washing and drying was repeated in order to remove excess catalyst. The product obtained is described in the following sections as Cat-A.

Method B
The MCM-41 nanoparticles were dried at 250 °C under flowing nitrogen and vacuum rounds. Subsequently, 0.5 g of dried MCM-41 was placed in contact with 1.5 mmol of MAO in a toluene suspension with stirring for 16 h. Then the solid was washed and dried

using the procedure already described for Cat-A. The dried particles were again suspended in toluene and contacted with the catalyst (0.5 wt% Zr) under stirring for 16 h, and finally the solid was washed and dried. The product obtained is described in the following sections as Cat-B.

Method C
The MCM-41 nanoparticles were dried at 250 °C as described in method B. A determined amount of dried MCM-41 were suspended in toluene and treated with ultrasound, in order to favor dispersion of the nanoparticles, for 5 min. Simultaneously, the required amount of catalyst was dissolved in 20 mL of toluene and then MAO (Al/Zr = 150) was added and the mixture was stirred for 15 min. An aliquot equivalent to the amount of the catalyst to be impregnated, which must be kept lower than the maximal Zr loading, was contacted with the particles suspended in toluene and left under stirring for 1 h at room temperature. After the impregnation, the solid was allowed to settle. A test of polymerization using the supernatant allows the presence of the Zr complex in the solvent to be discarded and to confirm in this way the efficiency of the impregnation procedure. The catalyst suspension can then be incorporated directly in the reactor without further washing and drying processes. This drastically simplifies the preparation of the supported catalyst and allows the amount of NMCM-41 charge introduced in the reactor for the preparation of the nanocomposites to be varied while keeping the total Zr amount introduced in the reactor constant. The catalyst prepared by this method is described as Cat-C.

Polymerization reactions
The polymerization reactions were carried out in a Büchi glass reactor of 1 L capacity equipped with a mechanical stirrer and a thermocouple. First toluene was introduced as solvent, followed by the co-catalyst (MAO).Then the system was saturated with propylene gas, and finally a given aliquot of catalyst solution in toluene, in the case of homogeneous polymerization, or a slurry of the supported catalyst was introduced into the reactor. Then, the pressure was adjusted to the desired value and the reaction was left under stirring at 1000 rpm for a predetermined time. The reaction was terminated by addition of 5% by volume of HCl/methanol 10 vol% solution. Then the polymer was precipitated with ethanol, filtered and washed before drying to constant weight.

Characterization
Molecular weights were estimated using a Waters Alliance GPC 2000 instrument at 135 °C. The polymeric microstructure was determined by ^{13}C NMR. The spectra were attained at 130 °C in a Varian Inova 300 operating at 75 MHz. Sample solutions of the polymers were prepared in *o*-dichlorobenzene and benzene-d_6 (20% v/v) in 5 mm sample tubes. Transmission electronic microscopy (TEM) images were obtained using a Philips Tecnai12 80 kV. The adsorption isotherms, Brunauer–Emmett–Teller (BET) surface areas and pore volumes of the silica samples were determined by N_2 adsorption–desorption at −196 °C in a Micromeritics ASAP 2010 equipment. The contents of zirconium fixed on the nanoparticles were determined by inductively coupled plasma emission spectroscopy (ICP) in a Perkin Elmer, Optima 7300V. TGA was performed on a TG 209-F1 Libre (Netzsch) at a scanning rate of 20 °C min^{-1} from 25 to 600 °C. The calorimetric analyses were carried out in a TA Instruments Q20 calorimeter at a heating rate of 10 °C min^{-1} from 25 to 160 °C.
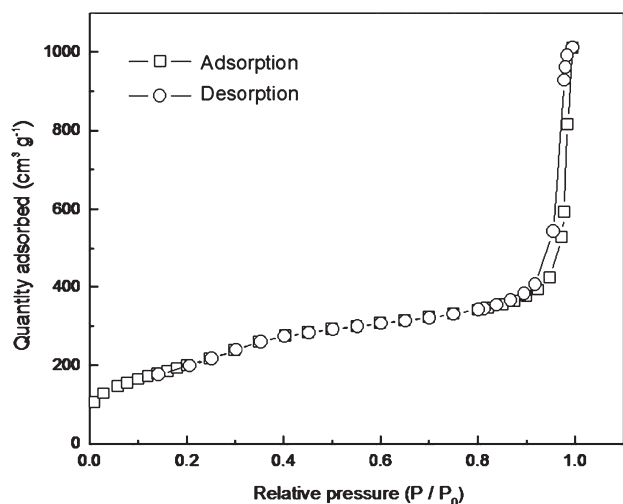
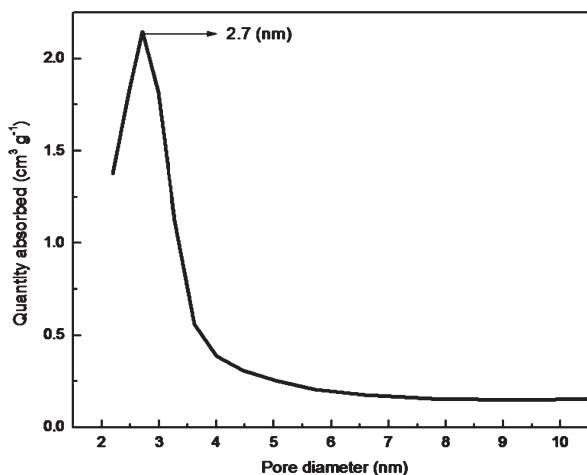**Figure 1.** Nitrogen adsorption isotherms for NMCM-41.

Table 1. Surface area and pore volume of NMCM-41

Surface area[a] ($m^2\,g^{-1}$)	Pore volume[b] ($cm^3\,g^{-1}$)	Pore diameter[b] (nm)
734	0.47	2.7

[a] Surface area obtained by the BET method.
[b] Parameters obtained by the BJH method.

Table 2. Results of impregnation for systems Cat-A and Cat-B

Catalyst	[Zr], expected (wt%)	[Zr], found[a] (wt%)	Impregnation yield (%)
Cat-A	0.7	0.43	61.4
Cat-B	0.5	0.36	72

[a] Concentration of Zr determined by ICP.

Figure 2. Size distribution of pore diameter for NMCM-41.

RESULTS AND DISCUSSION

Characterization of NMCM-41

The NMCM-41 was characterized by nitrogen adsorption analysis. The adsorption−desorption isotherms are presented in Fig. 1. The pore size distribution was obtained by the Barrett−Joyner−Halenda method (BJH) (Fig. 2). A small hysteresis can be seen from Fig. 1, indicating that the adsorption and desorption processes are very similar. This is characteristic of a mesoporous silica MCM-41 type which has channel-shaped pores.[20]

Figure 2 and Table 1 show that the pore diameter has a narrow distribution with a maximum value of the adsorbed volume corresponding to particles 2.7 nm in diameter and the surface area is very close to those reported in the literature for this type of material with nanometer particle sizes.[20]

Study of the methodologies for impregnation of Me$_2$Si(Ind)$_2$ZrCl$_2$ on NMCM-41

As mentioned before, the main purpose of this work was to develop a simple and optimized methodology for the *in situ* preparation of PP nanocomposites, leading to high activities and allowing control of the desired amount of filler and catalyst load on NMCM-41. To achieve this goal it was necessary to conduct studies of the impregnation methodologies to obtain an efficient catalyst for the polymerization of propylene.

Three different procedures for impregnation were studied. The systems called Cat-A and Cat-B were prepared by methods A and B, respectively. These differ in drying temperature and catalyst concentration. Impregnation yields were determined for both systems and the results are presented in Table 2. The impregnation methods A and B allowed the maximal Zr load on the NMCM-41 support to be evaluated, for the selected conditions.

The third method, Cat-C system, consists of using a pre-activated metallocene/MAO species for making the impregnation, minutes before adding the nanoparticles into the polymerization reactor. A much lower concentration of Zr was used in this case in order to ensure 100% yield of the impregnation. No catalytic activity was found on performing a polymerization test with the supernatant of the newly impregnated support, confirming that no dissolved catalyst exists in the homogeneous phase.

Scheme 1 shows the methodologies for impregnation of metallocene catalysts on NMCM-41.

The ICP analysis (Table 2) shows that the percentage of Zr found is less than expected for both systems. This indicates that the initial amount of Zr added exceeds the support maximal loading capacity, in the selected conditions. It may also be noticed that the Zr load on the support depends on the impregnation procedure. This was attributed to the distinct drying processes used, that may lead to a different distribution of silanols (isolated and vicinal) and siloxane groups that would affect the amount of MAO on the surface and subsequently influence the amount of Zr that can be supported.

Polymerization reactions

In order to select adequate conditions for the comparative study of these catalysts, preliminary polymerization runs were conducted for the homogeneous catalyst. The results for the polymerization of propylene in homogeneous phase are shown in Table 3, where variables such as temperature and reaction time were studied, showing the influence on the catalytic activity and molecular weight. These results show that a higher value of M_w can be reached at 25 °C allowing a material with good properties to be obtained.[21] Then these reaction conditions were established for the reactions with the supported catalysts.
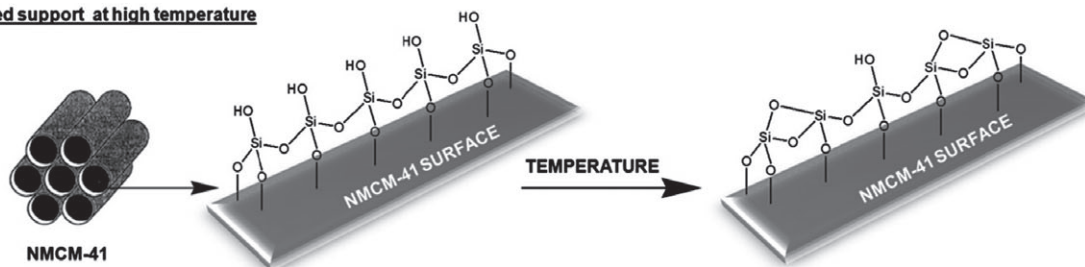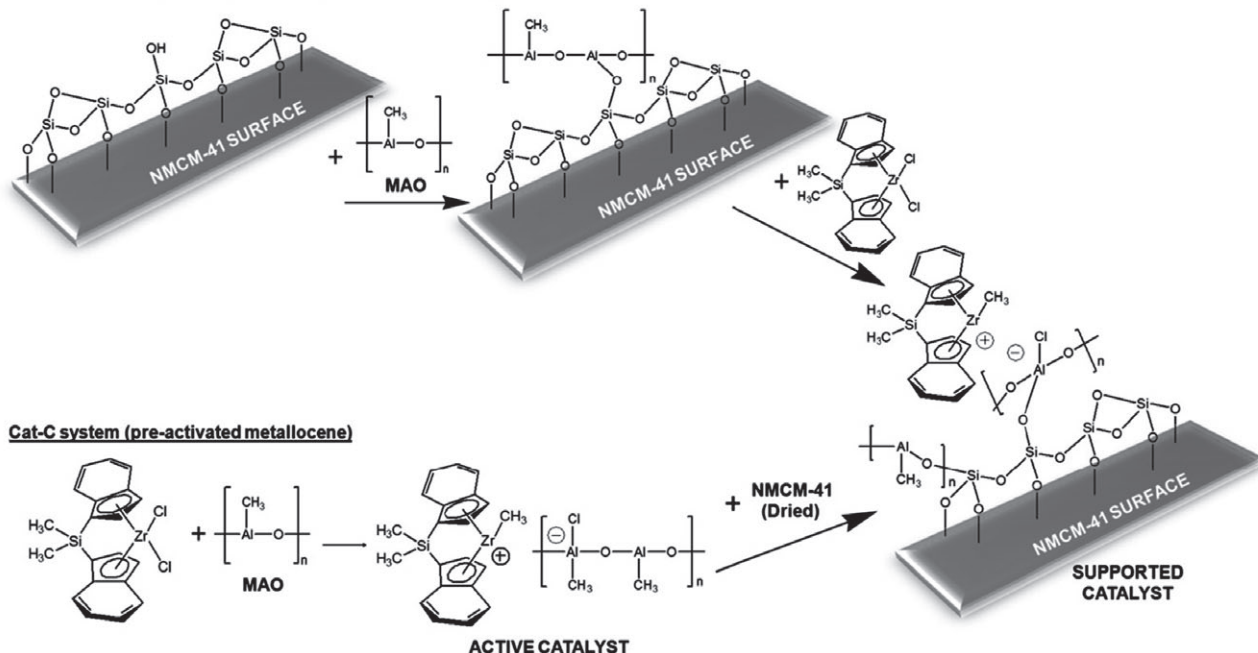
Scheme 1. Methodologies of impregnation for $Me_2Si(Ind)_2ZrCl_2$/NMCM-41.

Table 3.	Polymerizations of PP in the homogeneous phase					
Reaction	T (°C)	Time (h)	Yield (g)	Activity (kg$_{PP}$ n_{Zr}^{-1} bar^{-1} h^{-1})	M_w (g mol^{-1})	Tacticity m (mol%)
1	25	1	64	6290	111 300	96
2	40	0.5	64	12 700	71 000	95
3	50	0.5	128	25 140	53 300	96
Reaction conditions: $P = 2.5$ bar; volume 0.5 L; Al/Zr 1000; 4 µmol Zr.						

The polymerization behavior of the supported catalysts Cat-A and Cat-B was investigated next in order to study the effect of NMCM-41 as a support and to evaluate the influence on catalytic activity and on the molecular weight. The results are shown in Table 4. It can be seen that both catalysts show a decrease in catalytic activity compared to the homogeneous system (Table 3). This occurs because deactivation pathways may occur during impregnation, and not all of the supported catalyst on the surface of the NMCM-41 is in an active form to react with the monomer. Diffusional effects operating in the mesoporous MCM-41 nanoparticles could also contribute to the decrease of polymerization activity within the supported systems. Earlier studies on MCM-41 nanoparticles used as support for Cp_2ZrCl_2 in ethylene polymerization did not exclude that possibility.[20] However, it was reported that the differences in polymerization activity were more dependent on the surface chemistry than on diffusion constraints.

Regarding the supported systems it may be seen that Cat-A shows no significant variation in catalytic activity (Table 4). However, it shows the maximal activity at higher reaction temperatures, where molecular weights are lower. The polymerization yield increased on increasing the polymerization time but, when the higher yield was expressed in activity values, still no significant variation was observed.

Cat-B presents a lower amount of impregnated Zr but leads to a higher polymerization activity than Cat-A (Table 4). This can be attributed to the effect discussed above regarding the surface modification of the support that was dried at lower temperatures, which ultimately may make the catalyst more exposed on the surface and available to react. In addition the decrease of the Zr load on NMCM-41 may benefit catalyst activity by reducing potential deactivation pathways, namely the formation of inactive binuclear complexes. Therefore, we can

Table 4. Results of polymerizations with catalysts impregnated onto NMCM-41

Reaction	Catalyst	[Zr] (µmol Zr g^{-1} NMCM-41)	T (°C)	Time (h)	Yield (g)	Activity (kg$_{PP}$ n_{Zr}^{-1} bar^{-1} h^{-1})	M_w (g mol^{-1})	Tacticity m (mol%)
4	Cat-A	47	25	1	9.5	240	114 800	95
5	Cat-A	47	50	1	11.9	300	64 700	nd
6	Cat-A	47	50	1.5	17.3	290	61 800	nd
7	Cat-A	47	40	1.5	14.8	250	79 800	96
8	Cat-B	40	40	1	17.8	560	82 900	nd
9	Cat-B	40	25	1	17.1	550	121 300	96

Reaction conditions: $P = 3.4$ bar; volume 0.5 L; Al/Zr = 1000; mol of Zr Cat-A 12 µmol, Cat-B 9 µmol.

Table 5. Results of the polymerizations of propylene using catalyst Cat-C

Reaction	Zr (µmol)	[Zr] (µmol Zr g^{-1} NMCM-41)	NMCM-41 (wt%)[a]	Yield (g)	Activity (kg$_{PP}$ n_{Zr}^{-1} bar^{-1} h^{-1})	M_w (g mol^{-1})
10	5	12.5	5	13.1	1010	111 100
11	5	10	9.5	6.4	490	96 700
12	6	15	2.4	19.3	1280	110 400
13	6	12	4.4	12.6	830	100 900

Reaction conditions: $P = 2.5$ bar; volume 0.5 L; Al/Zr = 1000; $t = 1$ h; $T = 25$ °C.
[a] NMCM-41 (wt%) determined by TGA.

deduce that impregnation for Cat-B proved to be more adequate for the polymerization of propylene, not only because of its greater activity, but also because it leads to higher molecular weights, about 10 kg mol^{-1}, than those obtained in the homogeneous reaction at the same temperature. Finally, the tacticity is not affected significantly by use of these supported catalytic systems.

Preparation of nanocomposites by using Cat-C

The study of Cat-A and Cat-B allowed us to determine the loading capacity of the NMCM-41 nanoparticles. This permitted the preparation of the supported Cat-C system with optimized parameters such as drying temperature, and control of the catalyst concentration and the amount of support for the preparation of nanocomposites. By using this technique it was possible to reduce the impregnation time to a much lower value. Moreover, the washing and drying processes used in the preparation of Cat-A and Cat-B were eliminated, resulting in a greatly simplified procedure. Table 5 shows the results of polymerization tests performed with Cat-C.

The results show that significantly higher activities were obtained with Cat-C compared with previous catalyst supported
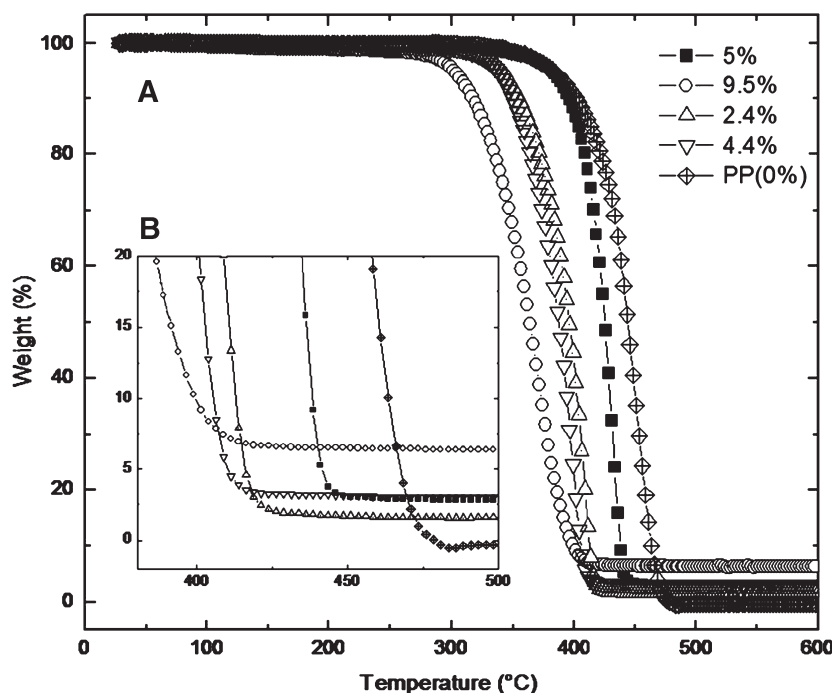
Figure 3. TGA of polymers obtained with Cat-C.
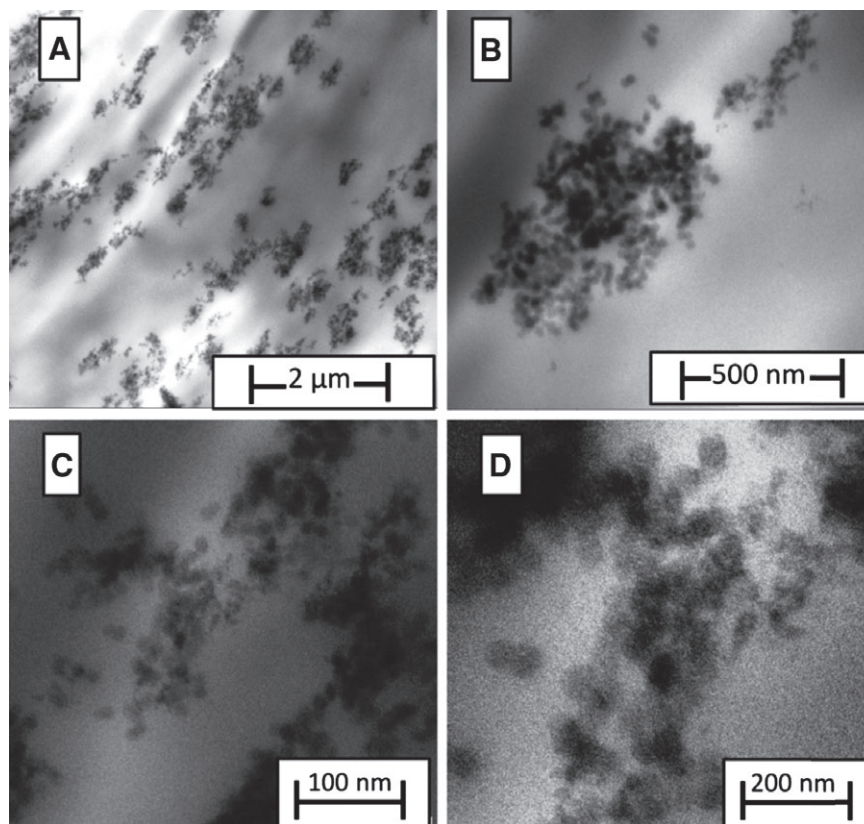
Figure 4. TEM images of PP/NMCM-41 (9.5 wt%) nanocomposites.

methodologies discussed earlier. Possibly the impregnation of NMCM-41 performed shortly before incorporation into the polymerization reactor and the removal of the washing and drying processes make the handling of the catalyst much simpler, which can avoid a possible catalyst deactivation. Additionally, the fact that the impregnation of NMCM-41 is made with a pre-activated metallocene/MAO species instead of impregnating the MAO pretreated support with the metallocene may provide a different environment for the active species, giving rise to different polymerization activities. Other aspects to be taken into account are the smaller impregnation time used and the significantly lower Zr loads of Cat-C which may affect catalyst distribution on the particle surface and potentiate active site isolation reducing potential bimolecular deactivation.

However, when the Zr load within Cat-C is reduced further from 15 to 10 μmol Zr g^{-1}, while keeping a similar concentration of Zr in the reaction medium, a decrease of activity is observed. This could result from a detrimental influence on activity when the optimal surface coverage needed to attain maximal activity is passed. As reported an earlier distribution of excessively distant active sites (as inferred from the lower metal loading) may result in a decrease of activity. On the other hand, when the amount of NMCM-41 charge is increased while keeping the concentration of Zr in the reaction medium constant, there is a decrease in catalytic activity (see reactions 10 and 11); this can be due to a deactivation of the catalyst in the presence of NMCM-41, but by increasing the concentration of the Zr slightly it is possible to obtain the largest amount of polymer (see reactions 12 and 13, Table 5).

As expected, this technique was appropriate for obtaining nanocomposites with different percentages of NMCM-41. This could be corroborated by the TGA presented in Fig. 3.

Table 6. Thermal properties of PP/NMCM-41 nanocomposites

Sample	NMCM-41 (wt%)	M_w (g mol^{-1})	T_m (°C)	T_c (°C)
PP	0	111 300	148	107
Cat-C	2.4	110 400	147	110
Cat-C	5	111 100	148	114

T_m and T_c values correspond to the second heating cycle of DSC analysis.

The TGA analysis shows some residues after decomposition (Fig. 3(B)), which corresponds to NMCM-41 incorporated in the PP matrix. The presence of MCM-41 nanoparticles in the composites shifts the onset of the degradation temperature to lower values (Fig. 3(A)). A decrease of about 100 °C is observed for 9.5% filler content. A similar behavior was previously observed for polyethylene/MCM-41 nanocomposites; it was shown that NMCM-41 played a role as promoter for polyethylene degradation.[10] This may be interesting if considered from the point of view of degradation of these polyolefins into basic petrochemicals to be used as feedstock or fuel for downstream processes after their service life.

Transmission electron microscopy

Figure 4 shows TEM images corresponding to a nanocomposite with 9.5 wt% of NMCM-41, where the dispersion of nanoparticles in the PP matrix is observed; in the first image (Fig. 4(A)) it is seen that the particles are distributed into small agglomerates within the polymer matrix. At higher magnifications (Figs 4(B), 4(C) and

4(D)), it is possible to distinguish each spherical particle unit with average sizes near 50 nm.

Thermal properties

Table 6 shows the thermal properties obtained by DSC for some nanocomposites prepared when using Cat-C. As can be appreciated the T_m is not affected significantly; however, the crystallization temperature T_c increases for higher loading rates which may be due to a nucleation effect induced by the NMCM-41 nanoparticles.

CONCLUSIONS

The MCM-41 nanoparticles used as support for metallocene in the polymerization of propylene were successfully incorporated in the PP matrix. The Cat-C system proved suitable for synthesizing these nanocomposites, achieving approximately 50% higher activities compared with the other tested methods while maintaining the value of M_w of PP around 100 kg mol^{-1}. Besides, the purpose of controlling the desired amounts of filler and catalyst loading was fulfilled.

ACKNOWLEDGEMENTS

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