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Ethylene polymerisation with zirconocene supported in Al-modified MCM-41: Catalytic behaviour and polymer properties

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Abstract

Heterogeneous olefin polymerisation catalysts were prepared by combining zirconocene with a series of purely siliceous and Al-containing MCM-41 supports with different Si/Al ratios, using simplified and improved versions of the well-known direct impregnation and "MAO pre-treatment" methods. The catalysts were tested in ethylene polymerisation. Analysis of polymerisation activities and kinetic profiles led to a rationalisation on the effect of support Si/Al ratios and methods used for catalyst preparation over the catalytic behaviour for ethylene polymerisations.

Polymers were characterised by scanning electron microscopy and differential scanning calorimetry. A mechanism is proposed to associate the formation or absence of fibrous morphology with polymerisation activities.

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1. Introduction

In recent years, several reports have shown how metallocene complexes can be combined with mesoporous materials of the M41S class to create very interesting supported catalysts for olefin polymerisation. Their unidimensional pores, larger than what is found in common zeolites, allow a better dispersion of the catalyst in the supports and better polymerisation activities [1,2]. Moreover, the confined space in the pores can regulate monomer insertion and chain growth [3,4], resulting in polymers with some rather unusual morphologies [5] and properties [6].

It is known that catalytic behaviour in these systems is influenced by the amount of Al present in the framework of MCM-41 and by the method used for catalyst preparation, which are mainly the direct impregnation and the MAO pre-treatment methods [7–9]. Experimental variables such as the amount of

methylalumoxane co-catalyst (MAO) in solution are also of central importance.

Pure siliceous MCM-41 is widely regarded as unable to fix the metallocene in an active form unless a pre-treatment with MAO is applied. This changes if aluminium is added to the MCM-41 structure. Rahiala et al. [10] first reported that the presence of aluminium in the framework of a MCM-41 support is beneficial for direct zirconocene catalyst fixation and leads to increased values of ethylene polymerisation activity, when compared with purely siliceous supports. Results obtained by Lee and his collaborators are in agreement with this finding [11]. These authors further added that the activities for catalysts prepared by direct impregnation of Al-MCM-41 outperform those obtained for catalysts prepared by MAO pre-treatment. However, Henriques et al. [12] observed a reverse trend, and report that MAO pre-treated supports originate catalysts with much higher activities, comparable to those of the homogeneous system. On the other hand Kaminsky et al. [13], using $Me_2C(Cp)(Flu)ZrCl_2$ supported by MAO pre-treatment in pure and Al-containing MCM-41, reported the presence of framework aluminium as detrimental to propene polymerisation activity.

A comparison of different studies is always difficult, as each research group uses different methods and experimental conditions to prepare the catalytic system and different polymerisation conditions, sometimes with apparently conflicting results.

This work intends to clarify the effect of framework aluminium and methods of preparation on the catalytic behaviour of zirconocene supported on MCM-41 carriers, using low/moderate MAO/Zr ratios. An improved method for catalyst preparation is proposed.

2. Experimental

2.1. Materials

Ethylene and nitrogen (Air Liquide) were purified through absorption columns containing molecular sieves 4A and 13X. Toluene (Petrogal) was dried by refluxing over metallic sodium, under nitrogen, and using benzophenone as indicator. Other materials were used without further purification. All sensitive reagents and materials were handled under nitrogen using standard inert atmosphere techniques.

2.2. Preparation and characterisation of the mesoporous solids

The detailed synthesis procedure of siliceous MCM-41 and aluminium-containing MCM-41 (direct synthesis) is described elsewhere [14]. Samples with different Si/Al ratios were prepared by adjusting the aluminium content in the synthesis gel. The template was partially removed by extraction with a solution 0.1 M NH_4NO_3 in 96% ethanol at reflux temperature for 2 h. After drying, the product was calcined under a flux of dry air at 550 °C for 10 h. The temperature was increased from 25 to 550 °C at 1 °C/min. The mesoporous solids were then stored in hermetic recipients inside a dessicator, until further use.

Powder XRD patterns were recorded on a Panalytical X'Pert Pro diffractometer using Cu Kα radiation filtered by Ni and a X'Celerator detector. The composition of the samples was determined by bulk chemical analysis (ICP and AAS). Nitrogen adsorption of the calcined samples was measured at −196 °C with an ASAP 2010 Micromeritics apparatus. Prior to the measurements, the samples were degassed at 350 °C for 3 h. The specific surface area was estimated by the BET method, and for the pore diameter, it was considered the average pore diameter determined by the relation $4V_{mes}/S_{BET}$, where V_{mes} is the mesoporous volume estimated from the N_2 adsorption isotherms. Microphotographs were obtained with a Hitachi S2400 scanning electron microscope (SEM) with a 25 kV electron beam.

The three aluminated MCM-41 supports have Si/Al ratios of 47, 30 and 16, as determined by bulk elemental analysis. These will be referred as M47, M30 and M16, for short. Purely siliceous MCM-41 will be referred to as MSI.

2.3. Preparation of the supported catalysts

Prior to use, each mesoporous solid is heated at 5 °C/min to 300 °C, with nitrogen purging (4 dm³/(g h)), and kept at this temperature for 2 h. After cooling, the solid is transferred and stored under nitrogen in a Schlenk flask, and used for catalyst heterogenisation according to methods A and B, detailed as follows:

2.3.1. Method A (direct impregnation)

0.5 g of the mesoporous solid is allowed to contact 25×10^{-6} mol of zirconocene (Aldrich, in the form of a solution 1.7×10^{-3} M, in toluene) for 16 h, in a Schlenk flask with magnetic stirring, concealed from ambient light. After this period of time, the catalyst suspension undergoes the clarified liquid test (see Section 2.3.3). If this test is passed successfully, the catalyst suspension is ready for use in the ethylene polymerisations. The catalysts designated as ZIR-M47, ZIR-M30, ZIR-M16 passed this test and present a metallocene load of $\sim 50 \times 10^{-6}$ mol/g. MSI was the only support unable to hold this metallocene load (clarified liquid test failed). Therefore, the catalyst derived from this support, ZIR-MSI was prepared using a new zirconocene solution diluted to 4.3×10^{-4} M, leading to a metallocene load of $\sim 13 \times 10^{-6}$ mol/g of solid. Additionally, mesoporous solid M47 was also impregnated with another metallocene load of 26×10^{-6} mol/g. The resulting catalyst is referred to as ZIR-M47L, and was used to confirm that activities are not influenced by variations in the zirconocene load of the support, as long as the total amount of Zr present in the polymerisation reactor is kept constant.

2.3.2. Method B (MAO pre-treatment)

0.5 g of the mesoporous solid is allowed to contacted 1.5×10^{-3} mol of MAO (Aldrich, 10% m/v in toluene, diluted to 0.12 M) at room temperature for 16 h, in a Schlenk flask with magnetic stirring. Next, the solid is washed three times with portions of ~ 20 ml dry toluene, and carefully dried in vacuum until the elimination of the solvent is complete. MAO pre-treatment load is equivalent to $\sim 3.0 \times 10^{-3}$ mol Al/g of support.

After drying, this MAO-treated solid is allowed to contacted the zirconocene in the conditions for method A, described above; 25×10^{-6} mol of zirconocene (1.7×10^{-3} M solution in toluene) is mixed for 16 h with the MAO-treated solid, then the catalyst suspensions undergo the clarified liquid test. The MSI solid did not show the limitation on adsorption capacity in contrast to method A. In fact, all the catalysts obtained from the MAO-treated mesoporous solids passed the clarified liquid test. Catalysts obtained by this method will be referred to in the next sections as ZIR-M47-M, ZIR-M30-M, ZIR-M16-M and ZIR-MSI-M.

Mesoporous solid M47 was also selected for preparation of a supported catalyst using an amount of MAO of $\sim 30 \times 10^{-3}$ mol/g in the pre-treatment step, that is, 10 times higher than that used for the other catalysts. This catalyst is designated as ZIR-M47-XM.

2.3.3. Clarified liquid test

In order to confirm that all the zirconocene is immobilised on the mesoporous solids, the catalyst suspension, obtained after 16 h contact between the support and the metallocene solution, is allowed to deposit the solids. Then a small volume of

Table 1
The supported catalyst systems prepared in this work

Catalyst	Support	MAO load in support (10^{-3} mol/g)[a]	Cp_2ZrCl_2 load in support (10^{-6} mol/g)
ZIR-MSI	MSI	–	13
ZIR-M47	M47	–	50
ZIR-M30	M30	–	50
ZIR-M16	M16	–	50
ZIR-M47L	M47	–	26
ZIR-MSI-M	MSI	3	50
ZIR-M47-M	M47	3	50
ZIR-M30-M	M30	3	50
ZIR-M16-M	M16	3	50
ZIR-M47-XM	M47	7	50

[a] Determined by chemical analysis.

Fig. 1. XRD diffractograms of the four mesoporous solids.

the clarified liquid (∼1 ml) is injected into the polymerisation reactor, where an adequate amount of MAO (same as used for the polymerisation runs) is already present. If any appreciable amount of polyethylene is formed, it means that this clarified liquid still contains zirconocene. Therefore, the fixation was not complete and the catalyst suspension must be rejected. The zirconocene/solid ratio will then be decreased for the catalytic system in evaluation, until the test is passed successfully.

Table 1 summarises the composition of the catalytic systems prepared. Each supported catalyst is obtained in the form of a suspension, containing a known volume of toluene and a known weight of solid, in a form of a very fine powder. Under vigorous agitation the solids can be easily dispersed leading to a homogeneous suspension. The zirconocene load in this solid is also known. In this way, zirconocene dosage for polymerisation runs can be easily carried out by careful volumetric measurements. In order to be sure of the reproducibility of this method and the quality of the results, each supported system is prepared more than once and tested several times (usually three times) for each set of polymerisation conditions.

2.4. Ethylene polymerisations and polymer characterisation

The polymerisation reactor consists of a $250\,cm^3$ bottle for pressure reactions (Wilmad LabGlass LG-3921), with crown cap and gasket, and a magnetic stirrer. This reactor is placed in a water bath with controlled temperature. Ethylene consumption rate is measured using two mass flow controllers (Hastings Instruments HFC-202 and Alicat Scientific 16 Series) and recorded in a personal computer with data acquisition hardware and software (a ComputerBoards CIO-DAS08/Jr-A0 interface card with Labtech DataLab software). Ethylene pressure is measured with a digital manometer (Air Liquide M2500) and also recorded.

The reactor is purged with vacuum/N_2 and loaded with enough toluene to match a total volume of $50\,cm^3$ when the polymerisation begins. Nitrogen is replaced by ethylene and the appropriate amount of MAO co-catalyst solution is injected into the reactor, in order to get Al/Zr ratios of 500 or 1500. Finally, catalyst suspension is vigorously stirred and the equivalent to
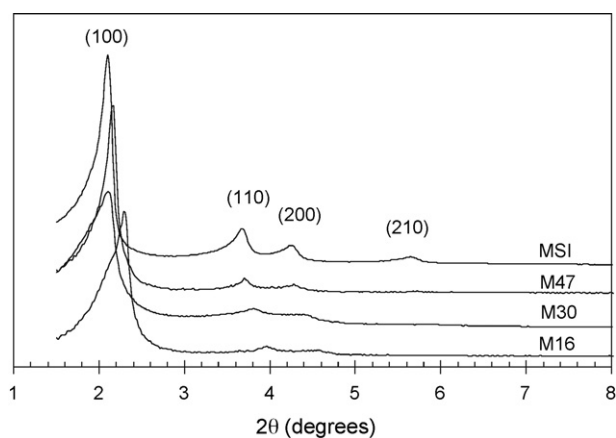
2×10^{-6} mol Zr is injected into the reactor by measuring an appropriate volume of this fine, homogeneous suspension. During the reaction, the temperature, pressure and ethylene mass flow data can be real-time monitored and stored. The ethylene mass flow has the units of SLPM (standard litre per minute) and is converted to ethylene consumption with the units kg PE/(mol Zr h.). The kinetic profiles correspond to ethylene consumption data versus time. The integral of the obtained curve in function of time corresponds to the average value of the activity, and agrees well with the weight of the recovered polymer. At the end the reactor is discharged and the polymer is precipitated over methanol acidified with HCl, and further washed twice with fresh methanol, before drying.

Polymer thermal analysis was performed with a TA Instruments DSC2980 with MDSC option, recording the second heating cycle, at $10\,^\circ$C/min. FTIR spectra were acquired on polymer films with a Perkin-Elmer 1600 FT-IR spectrophotometer. Morphology was analysed with a Hitachi S2400 scanning electron microscope (SEM) with a 25 kV electron beam.

3. Results and discussion

3.1. Characterisation of the mesoporous solids

Fig. 1 shows the XRD diffractograms obtained for the four mesoporous solids. Table 2 presents various structural parameters for these solids, as calculated from the XRD patterns and N_2 adsorption data.

Table 2
Structural parameters of the four mesoporous solids

Support	Si/Al	a_0 (Å)	S_{BET} (m²/g)	V_p (cm³ g⁻¹)	D_p (Å)
MSI	∞	48.7	1007	0.85	33.8
M47	47	47.2	975	0.80	32.8
M30	30	48.0	1057	0.87	32.9
M16	16	44.7	1092	0.82	30.0

a_0: unit cell parameter (calculated for a hexagonal symmetry as $a_o = 2d_{100}/\sqrt{3}$); S_{BET}: specific surface area; V_p: specific pore volume (calculated at the top of the adsorption step); D_p: average pore diameter ($D_p = 4V_p/S_{BET}$).
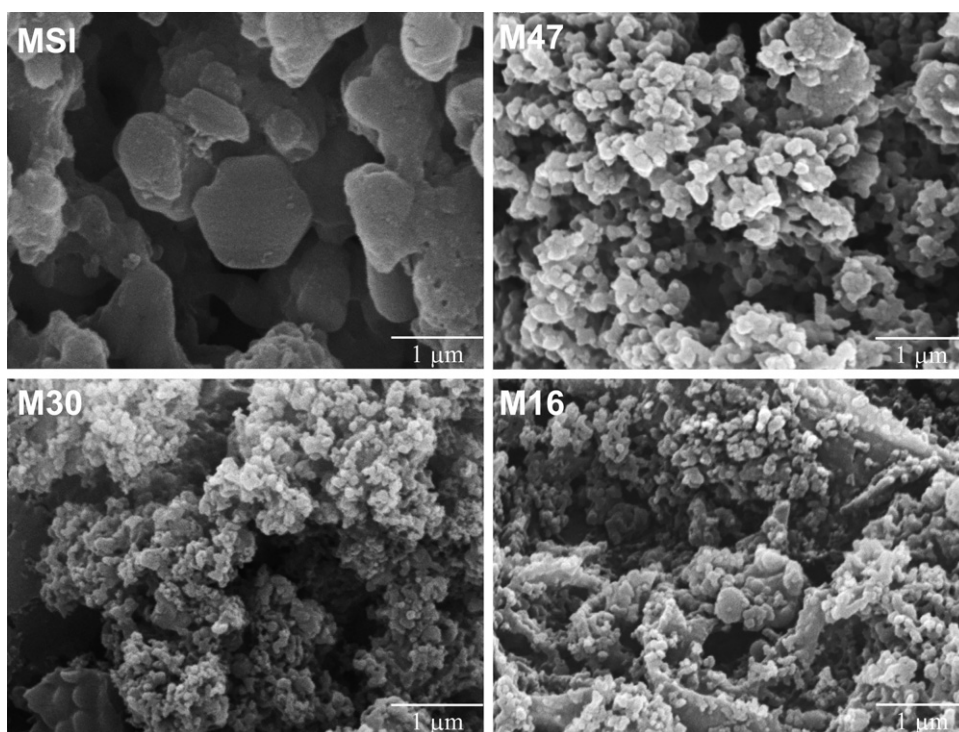
Fig. 2. SEM micrographs of the four mesoporous solids.

The diffractograms show that purely siliceous MCM-41 (MSI) presents better defined diffraction peaks. As the Al contents increases in the other three mesoporous solids, these peaks display a gradually lower intensity and shift to slightly higher 2θ angles. The SEM micrographs, in Fig. 2, present morphologies consistent with these results. A $20{,}000\times$ magnification shows large hexagonal aggregates for MSI, but not for M47, M30 and M16. Therefore, as expected, MSI is the mesoporous solid with higher structural regularity. For the remaining three mesoporous solids, the presence of aluminium causes a gradual distortion in their hexagonal structure. Nevertheless, the four MCM-41-type supports presented very similar structural parameters, which quantitatively differ by only $\sim$10%.

3.2. Preparation of the catalytic systems

Two methods widely used for the heterogenisation of single-site polymerisation catalysts over siliceous solids are the "direct impregnation" and the "MAO pre-treatment" methods [7–9]. In the final steps of a typical implementation of these procedures, the support is allowed to contact a solution containing a given load of some transition metal catalyst, which may go well beyond the adsorption capacity of the support. Excess catalyst remaining in the resulting suspension is removed by repeated washing with fresh solvent, and finally the solvent is also removed, usually in vacuum. This leaves a dry solid saturated with the transition metal compound adsorbed on it. For a variety of supports or catalysts, the adsorption capabilities will be different and the supports will retain different amounts of catalyst. Therefore, the catalyst content for each support must be determined by spectroscopic analysis (usually ICP-AES), in order to calculate Al/Zr ratios and the corresponding polymerisation activities.

Overall, the procedure for catalyst preparation and use looks problematic and time-consuming, above all if a large number of different catalytic systems must be prepared. In the procedures developed for this work, the catalyst load is kept below the saturation limit of the mesoporous solid. This way, washing the solid is unnecessary and the amount of catalyst to be used in polymerisation can be directly measured, eliminating the need for the elemental analysis and allowing a simpler implementation. Furthermore, the number of manipulations to be performed on the catalyst suspensions is greatly reduced, protecting the sensitive organometallic compounds from premature deactivation. Different catalytic systems, obtained with different carriers, can be prepared and immediately used for a series of polymerisation runs with constant metallocene load, thus making possible an immediate direct comparison of the results. It is only required that when performing the clarified liquid test, no polymer is formed.

When method A was used for catalyst heterogenisation, ZIR-MSI was the sole catalytic system which initially did not pass the clarified liquid test successfully for the zirconocene load chosen, 50×10^{-6} mol/g. Therefore the amount of support had to be increased four-fold leading to a lower zirconocene load of 13×10^{-6} mol/g. This was also the catalytic system where no aluminium was present inside the mesoporous structure. This result shows how the presence of framework aluminium strongly increases the zirconocene retention capacity for a siliceous solid, in agreement with data reported by Rahiala et al [10].

For method B the MAO pre-treatment was performed using a small MAO load, equivalent to 3.0×10^{-3} mol Al/g, in order

to avoid excessive pore blocking in the mesoporous solid. However small, this load represents an amount of aluminium several times higher than what is already present in the framework of the mesoporous structures. The solvents collected after washing the series of MAO-treated solids did not show any traces of fumes or precipitates. This suggests that MAO fixation to the mesoporous solid was complete, and in fact the bulk elemental analysis later performed on the MAO-treated solids did confirm the result.

In the subsequent impregnation of the MAO-treated supports with zirconocene, the same load of Zr (50×10^{-6} mol/g), as for method A, was used. It was found that all the four MAO-treated mesoporous solids fully adsorbed the organometallic compound. The MSI solid prepared by method B did not show the limitation on adsorption capacity observed with method A. This data strength the beneficial role of aluminium on the retention capacity of the siliceous solid, irrespective of the way used for its addition (in situ modification of siliceous MCM-41 or post-pre-treatment of the support with MAO).

3.3. Ethylene polymerisations

Ethylene polymerisations were performed with 2×10^{-6} mol zirconocene in the presence of MAO at low and moderate Al/Zr ratios, 500 and 1500. Fig. 3 shows typical kinetic profiles, obtained for a series of catalytic systems prepared according to method A. The data shown for each supported system is the result of three independent polymerisation tests carried out under the same experimental conditions. Experiments show very good reproducibility.

Integration of each kinetic profile over the duration of the polymerisation run gives the average polymerisation activity of each polymerisation run. Next an arithmetic mean of the average polymerisation activities obtained for each catalyst, under the same conditions, is calculated. Results obtained for the eight supported catalysts, prepared according to methods A or B are compared in Fig. 4.

Polymerisation activities obtained for ethylene using homogeneous Cp_2ZrCl_2/MAO system present an average value around 7000 kg/(mol Zr·h), at Al/Zr = 500, room temperature
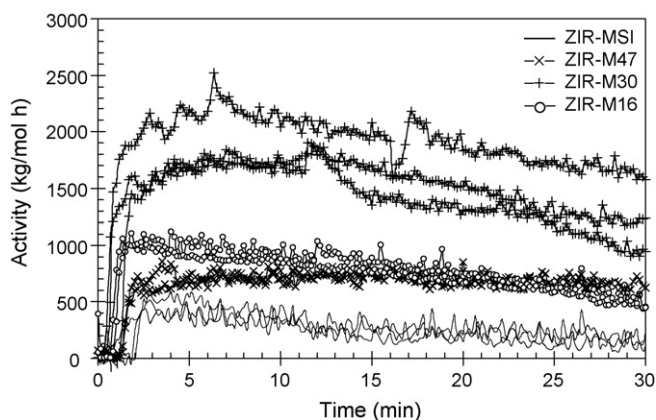

Fig. 3. Set of kinetic profiles obtained for the ethylene polymerisation runs performed with the catalytic systems prepared with method A, for Al/Zr = 500.
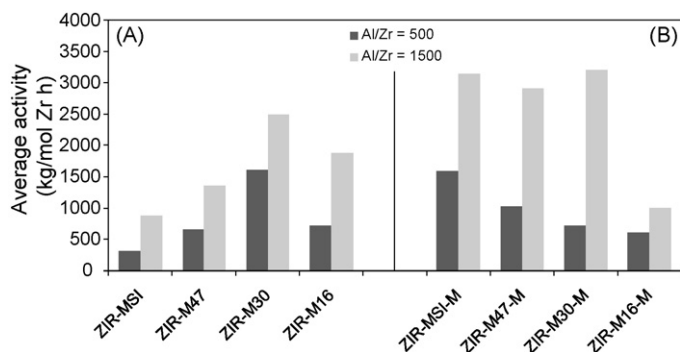

Fig. 4. Average polymerisation activities obtained for the catalytic systems in study (Zr contents: 2.0×10^{-6} mol; temperature: 25 °C; ethylene pressure: 1.2 bar abs; total volume: 50 cm^3).

and 1.2 bar abs ethylene pressure. The best results obtained with the supported systems using the same conditions are near 1600 kg/(mol Zr·h), a good accomplishment taking into account the small Al/Zr ratio and the low ethylene pressure used. Raising the amount of MAO to Al/Zr ~ 1500 greatly increases the productivity for all the catalytic systems.

When using method A (Fig. 4A), all the catalysts derived from the aluminated supports, ZIR-M47, ZIR-M30 and ZIR-M16, perform better than the one derived from the pure siliceous support, ZIR-MSI. The presence of aluminium not only favours the fixation of the zirconocene, as stated above, but also the interaction between Zr and the framework acidic Al seems advantageous to the formation of the active centres. Nevertheless, a very high Al contents turns out to be detrimental to catalytic activities. This suggests the existence of an optimum surface acidity level beyond which zirconocene becomes unable to drive efficiently the polymerisation of ethylene. These results are consistent with the observations by Sano et al. [15] and Miyazaki et al. [16]. They activated a metallocene catalyst with metal-MCM-41 (metal = Al, Zn, Ga), using triisobutylaluminium as alkylating agent and reported a maximum for propylene polymerisation activity at an intermediate Si/metal value ~13 [16].

When method B is used (Fig. 4B), the catalyst obtained with pure siliceous support, ZIR-MSI-M, is the most active. A gradual introduction of aluminium in the supports causes the activity to decrease.

In order to explain this behaviour, one can imagine that the MAO from the pre-treatment may add more acidic Al centres to the solid, through the TMA (trimethylaluminum) presence [17,18], as demonstrated by Anwander et al. [19]. But on the other hand it may reduce the effect of framework Al and consequently the acidity differences between the supports. Therefore, the final support acidity will be the result of both aluminium contributions: from MAO and from the mesoporous structure. Now, catalysts with Al contents still below the optimum acidity will increase their activity relative to method A, while other catalysts will exceed this optimum and their activity decreases. Fig. 5 summarizes these conclusions, showing the increments in the polymerisation activities when switching from method A to method B.
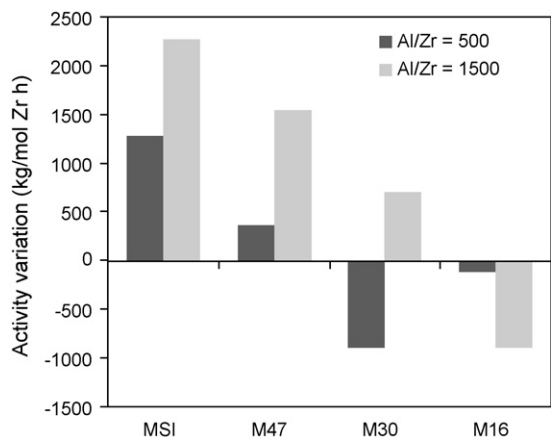
Fig. 5. Variations observed in polymerisation activities when switching from method A to method B.

This explanation is consistent with additional tests performed with support M47 treated with a great excess of MAO in the pre-treatment step (catalyst ZIR-M47-XM). After washing and drying, bulk elemental analysis reported a final Al content of 7×10^{-3} mol/g in this MAO-saturated support. Fig. 6 compares the activities for polymerisation runs performed with the catalysts resulting from support M47. Activities are clearly higher when lower MAO loads are used in the pre-treatment of the support, but very high MAO loads decrease the polymerisation activity.

The conclusions from Figs. 5 and 6 are that pre-treating a support with MAO prior to fixation of the metallocene, method B, can increase or decrease polymerisation activity, relatively to method A. It depends on the Si/Al ratio of the initial support and on the MAO load used on the pre-treatment. Method B is only satisfactory for pure siliceous MCM-41 or for supports with low Al contents, but high MAO loads should be avoided. While the discussion above is clearly a simplistic interpreta-
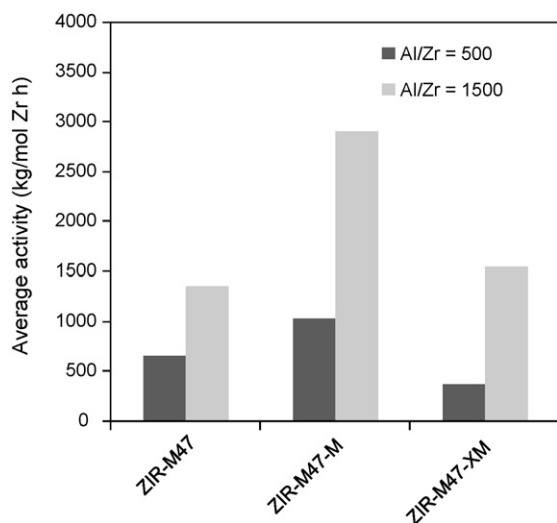

Fig. 6. Ethylene polymerisation activities obtained for catalysts derived from support M47 and prepared with: method A (ZIR-M47); method B, 3×10^{-3} mol MAO treatment (ZIR-M47-M); method B, 30×10^{-3} mol MAO treatment (ZIR-M47-XM).
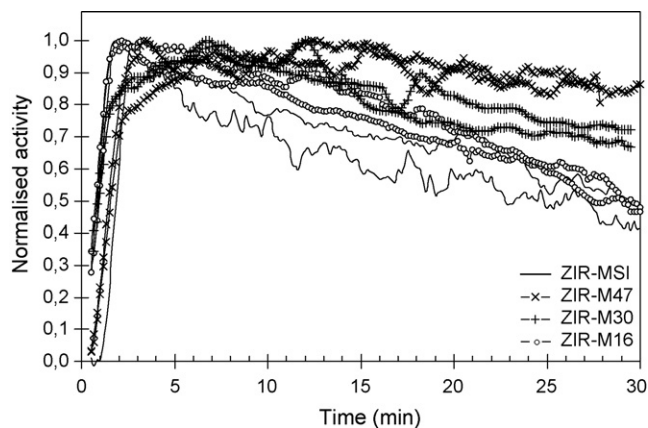

Fig. 7. Normalised kinetic profiles for the ethylene polymerisation runs performed with the catalytic systems prepared with method A, for Al/Zr = 500.

tion of the effects of the support composition and method of preparation, it can explain some conflicting results found in open literature, and already mentioned in the introduction. For instance the low activities of the catalysts derived from MAO pre-treatment, relatively to the direct impregnation method [11] may be the result of the high amounts of MAO used in the support pre-treatment step (20×10^{-3} mol/g support) while the opposite results, reported by Henriques et al., may be explained by the use of a much lower amount of MAO (2.5×10^{-3} mol/g support) [12].

The Si/Al ratio was also found to play an additional positive effect on polymerisation activity through its influence on the active centres stability. Fig. 7 presents the normalised kinetic profiles for the catalytic systems prepared with method A. This normalisation allows an easier examination of the deactivation rates in a set of polymerisation runs.

Data shows that the aluminium-free supported catalyst, which presents the lowest activity, leads to the fastest decay in ethylene polymerisation activity (catalyst ZIR-MSI). When a small amount of aluminium is present in the support (catalyst ZIR-M47), this decay is almost absent. However, high aluminium contents in the support (systems ZIR-M30 e ZIR-M16) causes the decays to rise to a level close to the pure siliceous systems.
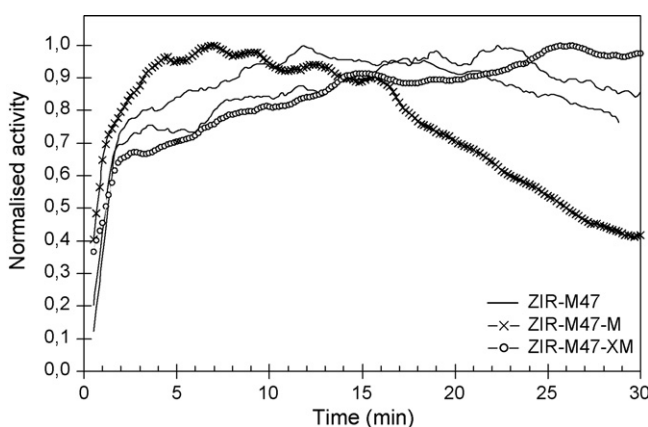

Fig. 8. Normalised kinetic profiles for the ethylene polymerisation runs performed with catalytic systems derived from support M47, for Al/Zr = 1500.
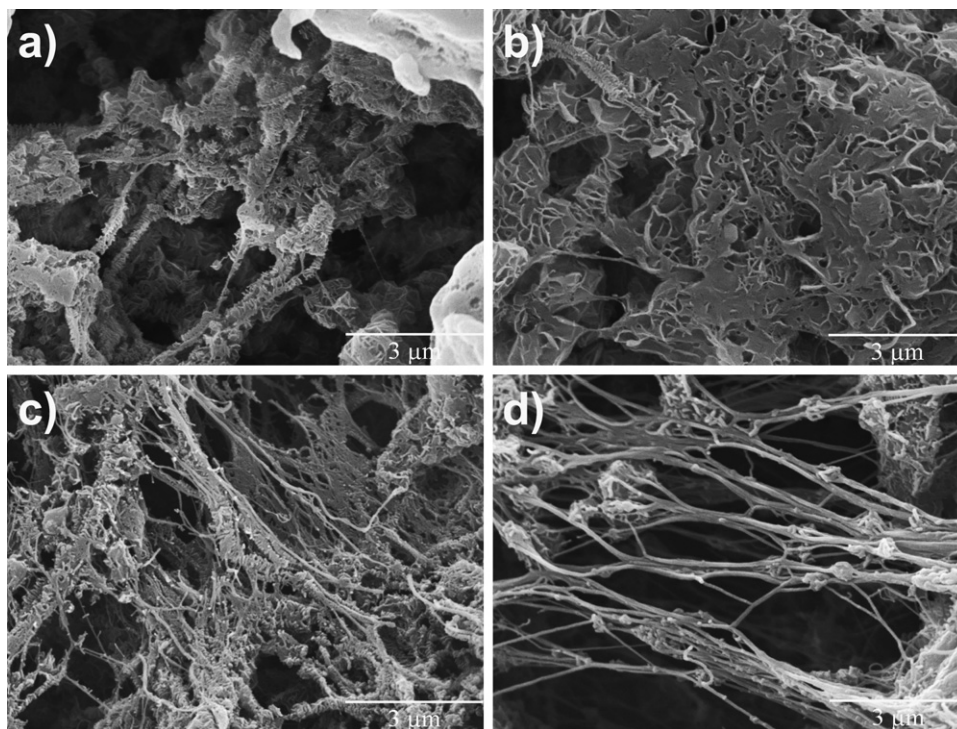
Fig. 9. SEM micrographs for the polyethylenes obtained with: (a) solution polymerisation; (b) ZIR-M30, 1900 kg/(mol Zr·h); (c) ZIR-M47, 670 kg/(mol Zr·h); (d) ZIR-M16, 120 kg/(mol Zr·h).

The aluminium content in the support has therefore a strong influence in the catalyst stability.

A similar behaviour is observed when changing from method A to method B. However, the slopes of the normalised kinetic profiles seem a little more pronounced, suggesting a higher deactivation rate of the active sites for catalysts pre-treated with MAO.

Fig. 8 presents the set of normalised kinetic profiles for the experiments performed with catalysts prepared with mesoporous support M47 at higher Al/Zr ratios. Using preparation method A with this support (catalyst ZIR-M47) and raising the co-catalyst ratio to Al/Zr ∼ 1500 it is possible to achieve very stable kinetic profiles. The same effect is observed when switching to preparation method B and using the MAO saturated support (catalyst ZIR-M47-XM). While the acidic properties achieved at high MAO contents are not beneficial to polymerisation activity, the MAO saturated surface seems to play a stabilising effect on the existing active centres. However, a strong deactivation cannot be avoided for the most active polymerisations, those combining the catalyst prepared following method B (ZIR-M47-M) and Al/Zr ∼ 1500.

3.4. Polymer characterisation

The polyethylenes were obtained as common macroscopic flakes. SEM analysis showed the presence of fibres when focusing inside the various fissures present at the surface of the macroscopic particle (Fig. 9). The very high specific surface area
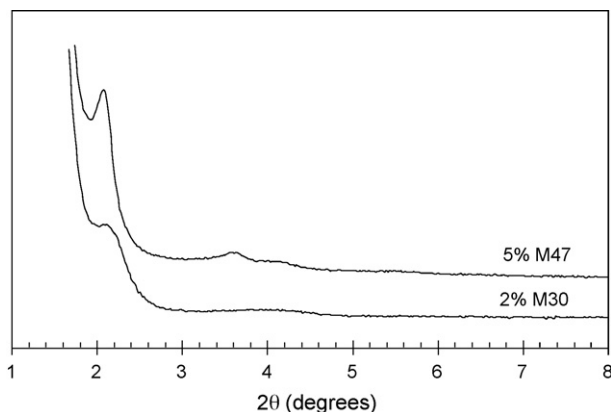

Fig. 10. Low-angle XRD diffractograms for films of polyethylene obtained with high activity catalysts and containing small amounts of support.
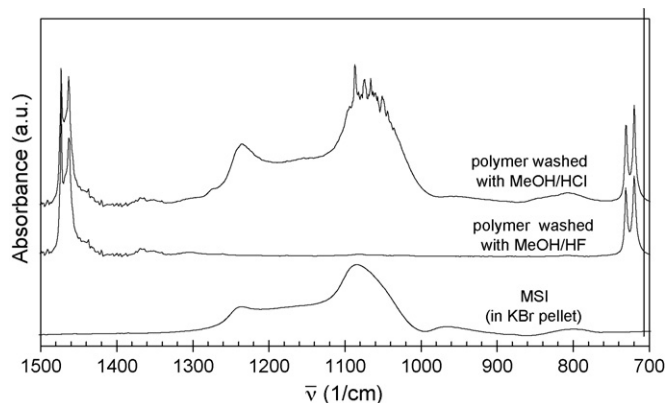

Fig. 11. Typical FTIR spectra for a polyethylene synthesised with the supported catalysts and for the MSI support.
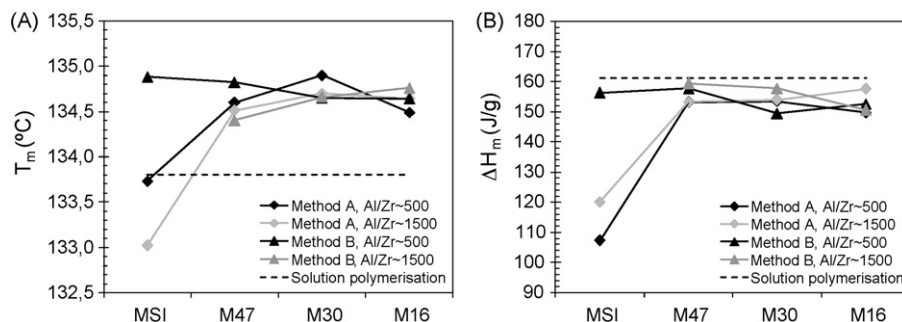
Fig. 12. Variations in melting temperatures (A) and enthalpies (B) for representative polyethylene samples.

of the supports and the low Cp_2ZrCl_2 loads used should favour the distribution of this catalyst predominantly inside the pores of the support particles, with a lesser amount present in the external surface. Formation of fibres by extrusive polymerisation [5] is thus favoured. The formation of fibres is not correlated with the Si/Al ratio of the support. The method used for the preparation of the catalyst had no influence in this aspect either. For polymer samples obtained with catalyst ZIR-M47-XM, a fibreless morphology was observed, probably because the pores of the support were blocked with the high MAO load used in the preparation of the catalyst.

Polyethylene samples obtained with lower activities presented better distinguishable fibres. These results suggest that the confinement effects are lost for high polymerisation activities. The rupture of the support nanotubes by action of the many chains pressed inside could account for this fact. Nevertheless, XRD analyses of PE samples containing support residues suggest that the structure of the support is retained, at least to some extent, after polymerisation (Fig. 10).

An additional explanation for the formation or absence of fibres may reside in the rate of chain formation and the easiness with which the chains extrude through the pores. The nanotubes tend to orient chains to a straight grow. Depending on catalyst activity, the polyethylene chains will grow up at different rates. For lower activities, these chains grow slowly and attain a more relaxed conformation, which is kept once the exterior of the pore is reached. Then various parallel chains may join together and produce fibres. On the other hand, very active catalysts produce chains which grow up faster but may get squeezed due to friction on the confined space. When these chains reach the exterior of the pore, their tension is released suddenly but the absence of a mould makes them stretch to a disordered conformation, preventing the formation of fibres.

The polyethylenes synthesised with the supported catalysts were analysed by FTIR. Fig. 11 presents the typical FTIR spectra for these polymers, in the fingerprint region. The spectrum of the MSI support is also shown. The intense absorption bands present (1078 and $1234\,cm^{-1}$) are characteristic of Si–O–Si structures. Thus, polyethylene samples may contain unremoved catalyst support, even with the conventional MeOH/HCl washing. The inorganic support can however be removed if using MeOH/HF instead. In the literature, no comparable observation was mentioned before (and its consequences investigated) possibly because in many of these cases the amount of support

in the polymer was considered negligibly small. Turunen et al [20] suggested that co-catalyst residues can remain in the polymers obtained in this type of polymerisations, but FTIR results showed this was not the case.

In Fig. 12 melting temperatures and enthalpies of the polyethylene samples are charted as a function of the support used for catalyst heterogenisation. The two methods of preparation and the experimental conditions are also accounted for.

As usual, melting temperatures of the polyethylenes synthesised with the mesoporous catalysts are slightly higher than homogeneous analogous ones, probably due to the formation of high molecular weight polymers and/or extended chain crystals [21]. For catalysts synthesised from Al-containing supports no direct correlation was found between the Si/Al ratio of the supports, the method of preparation or the co-catalyst Al/Zr ratio and either the melting temperatures or enthalpies. However, catalysts synthesised from pure siliceous support using method A exhibit significantly lower melting temperatures and enthalpies. These observations may be accounted for by a dilution effect due to the presence of support residues and/or to the formation of a hybrid material with distinct properties. This will be the subject of forthcoming studies.

4. Conclusion

The experimental procedure presented in this work was aimed on simplifying and improving the preparation of the catalyst for ethylene polymerisation. The ability to control catalyst dosage is very useful when the experimental results for many different catalysts are compared, but is seldom found in this type of experiments.

Our results allow a rationalisation on the effect of support Si/Al ratios and methods used for catalyst preparation over polymerisation activities and catalyst stability. Under the experimental conditions used, zirconocene supported on neat, aluminium-free MCM-41 is active in ethylene polymerisation. However, low activities and fast catalyst deactivation are observed. Aluminium in the framework of MCM-41 improves the fixation of zirconocene, allowing the preparation of catalysts with higher Zr loads. An optimal value of Si/Al must be achieved for maximum polymerisation activity. Too low Si/Al ratios are not favourable. Framework aluminium plays an important role on catalyst stability. Low amounts of Al are beneficial but further increase reduces the stability.

The use of aluminium modified MCM supports with optimised Si/Al ratio allows the preparation of high activity supported catalysts, without the need for performing a MAO pre-treatment.

Modification of supports, by prior impregnation with MAO, reduces the effect of framework acidity. This preparation method is only suitable for pure siliceous or high Si/Al supports.

The chemistry of the support and the method of preparation do not cause specific effects over polymer morphology, but can influence it indirectly, due to their impact on activity. Low activities seem to favour the usual fibrous morphology.

The presence of unremoved catalyst support in the bulk of the polyethylenes has important consequences over polymer properties. This subject is now under investigation and will be the focus of forthcoming reports.

Acknowledgments

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