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Ethylene polymerization catalyzed by metallocene supported on mesoporous materials

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Summary

In this work, different mesoporous materials were employed for the preparation of supported metallocene catalysts to be evaluated in ethylene polymerization and their performance was related to the chemistry of the materials surface used as support. The supports employed were MCM-41, SBA-15 and mesoporous TiO_2. The performance of the prepared catalysts was compared with the homogeneous catalyst precursor system. Those mesoporous materials, as well as the prepared metallocene catalysts, were analyzed by infrared absorption spectrometry (FTIR). Polymers were also characterized by FTIR, for the determination of the number-average molecular weight, and by differential scanning calorimetry (DSC) to determine thermal characteristics of the produced polyethylene. Among the studied metallocene supported catalysts, the one based on the mesoporous support SBA-15 achieved the highest activities, almost as high as that observed for the homogeneous system.

Introduction

The majority of the studies on heterogeneous metallocene catalysts for olefin polymerization are associated with the use of silica as support material. However, several carriers have already been used for the fixation of metallocene complexes to prepare catalyst systems [1-6] in order to allow the use of those heterogeneous systems in mass or gas-phase production processes. Recently, materials that possess large and ordered pores diameter, as in the cases of MCM-41 and SBA-15 [7,8] have gained growing interest.

In a previous investigation, Wang and co-workers [9] employed bis(cyclopentadienyl) zirconocene (Cp_2ZrCl_2) supported on MCM-41 for ethylene polymerization. They have observed that the supported catalyst presented elevated activity, and also the produced polyethylene possessed higher melting temperatures than that of the polymer obtained with the homogeneous corresponding system in the same reaction conditions. Comparing the polymers synthesized at different polymerization times, they also found that the melting temperature was similar with the extension of polymerization and Tm of the first scan was also similar to the second scan.

In another work in the literature [10], the metallocene complex Cp_2ZrCl_2 was supported on mesoporous type MCM-41 material containing aluminum species in its structure (Al-MCM-41) and was evaluated in the synthesis of polyethylene using methylaluminoxane (MAO) in the reaction medium as cocatalyst. The activities of the zirconocene catalysts supported directly on Al-MCM-41 were comparable to those of the catalyst prepared by chemically modifying the support before zirconocene fixation. The authors observed that the activity obtained with the first supported system was much higher than that of the catalyst supported on Al-MCM-41 modified by reaction with MAO before the metallocene impregnation. Parameters like SAR (Si/Al ratio in the material framework) and the previous chemical treatment received by the support should be taken in consideration to explain the different behaviors observed in the performance of the catalysts supported on those materials. When Cp_2ZrCl_2 was supported on MCM-41 and Al-MCM-41 for ethylene polymerizations, the authors evidenced that MCM-41 generated active catalysts only when the support received chemical treatment with MAO, while Al-MCM-41 can be used without previous treatment. However, the increase of SAR in Al-MCM-41 resulted in a decrease of catalyst activity.

The aim of the present work was to evaluate the performance of dimethyl silyl bis (indenyl) zirconocene-based catalyst in ethylene polymerization as homogeneous system, and to compare its behavior with those of the catalysts supported on the mesoporous materials MCM-41, SBA-15 and mesoporous TiO_2. The influence of the surface chemistry of those materials was also investigated and related with the catalyst activity, taking into consideration the surface modification on the supports with methylaluminoxane (MAO). Moreover, the cocatalyst type introduced in the polymerization medium was also modified by the use of a mixture of MAO and triisobutyl aluminum (TIBA), in order to evaluate the use of a lesser amount of the expensive aluminoxane in the reaction medium.

Experimental

Materials

Operations were carried out under nitrogen using Schlenk techniques. Ethylene and nitrogen were purified by sequential passage through columns containing 4 A molecular sieves and copper catalyst to remove oxygen, carbon dioxide and moisture, respectively. Toluene was refluxed over metallic sodium/benzophenone and was distilled under a nitrogen atmosphere prior to use. MAO (Methylaluminoxane) (10 wt.% solution in toluene), TIBA (Triisobutylaluminium) and rac-$Me_2Si(Ind)_2ZrCl_2$ (rac-dimethyl silyl bis (indenyl) zircononium dichloride) from Crompton Corp, Germany, were used without further purification. Mesoporous MCM-41 and TiO_2 previously heated to eliminate templates and characterized to confirm its structure were kindly purchased from the Catalysis Laboratory at UFRN and the Department of Chemistry and Biochemistry at University of Windsor.

Synthesis of SBA-15

The chemicals used to synthesize SBA-15 were triblock copolymer (Pluronic P123) – poly (ethylene oxide) – poly (propylene oxide) – poly (ethylene oxide) -

$EO_{20}PO_{70}EO_{20}$ from BASF Co. (Mav = 5750 g mol-1) as a template, hydrochloric fuming acid 37% from Merck, distilled water and tetraethyl orthosilicate (TEOS) from Aldrich. The reactants were mixed in order to obtain a gel of the following molar composition: 1 TEOS: 0.017 P123: 5.7 HCl: 193 H_2O. To prepare SBA-15 sample, 2.4 g of P123 copolymer was dispersed in solution prepared with 14 g of HCl and 79.7 g water, under stirring at 35° C. After complete dissolution of P123, 5.3 g of TEOS were added. The mixture was aged for 24 hours, to obtain a homogeneous gel. The reaction mixture was hydrothermally treated under autogeneous pressure at 373 K for 48 hours. The resulting products were filtered, washed with distilled water and 2% HCl/EtOH solution, and dried at room temperature [11]. The material was characterized by FTIR, XRD and TGA to confirm its structure and template removal.

Support thermal treatment

In order to remove possible moisture before metallocene impregnation, MCM-41 and SBA-15 were heated again from room temperature to 400° C at a heating rate of 5°C min-1 and this temperature was maintained for 4 h under nitrogen flow. Mesoporous titanium oxide was used directly for the catalyst preparation.

Catalyst preparation

SBA-15, TiO_2 and MCM-41 were pretreated with MAO taking 1 g of the mesoporous materials and adding 20 ml of toluene and 5.8 ml of methylaluminoxane (toluene solution of MAO, 10 wt.%). The suspension was stirred for 4 h at room temperature and afterwards, the solid was washed three times with 40 ml of toluene at 90° C and dried by nitrogen flow. Subsequently, a toluene rac-$Me_2Si(Ind)_2ZrCl_2$ solution was added to the mesoporous materials and this suspensions was stirred for 4 h. Then, the colorless supernatant was removed with syringe and the system was dried under nitrogen flow until constant weight.

Polymerization

Homogeneous ethylene polymerization was carried out in a 1000 ml glass reactor. Toluene, MAO toluene solution ([Al]/[Zr] = 1000) or a mixture of MAO and TIBA toluene solution ([Al]/[Zr] = 100 and 500, respectively), was introduced into the reactor followed by ethylene saturation at 2 bar. A toluene solution of the metallocene was then injected into the reactor, initiating the polymerization. The reaction was terminated after 1 h by interrupting ethylene feed and adding a 5% HCl/methanol solution to the reaction medium. The precipitated polymer was filtered, washed and dried at 60°C.

The heterogeneous polymerization was also carried out in a similar way as the homogeneous one. After charging the reactor with toluene, MAO or MAO/TIBA solution and ethylene, a suspension of the supported catalyst in toluene was then injected into the reactor, starting the polymerization.

Catalyst characterization

The chemical characteristics of the supports surface were evaluated through Fourier Transform Infrared Spectroscopy (FTIR).

The analyses performed in this work intended to qualitatively evaluate the presence of hydroxyl groups on the surface of the materials employed as supports and of its reaction after the catalysts preparation (metallocene impregnated on the supports). The samples were prepared in nujol suspension and apply in a KBr cell for gases. The spectra were obtained in the range from 4500 to 400 cm^{-1}.

Polymer characterization

Differential scanning calorimetric analyses (DSC) were used to determine the melting temperature and degree of crystallinity. The analyses were carried out in a Perkin Elmer DSC7 in the temperature range of 60 to 180º C by heating rate at 10º C/min. The degree of crystallinity were determined at the second scan and using ΔH^o ethylene = 293 J/mol.

Absorption infrared spectroscopy was employed to determine the concentration of unsaturated end groups in the polymer chain to estimate the number average molecular weight $\langle M_n \rangle$ of the obtained polyethylene. Polymer films were prepared in a hydraulic press at 180º C and 5,000 kgf/cm^2 and analyzed in the FTIR spectrometer. Spectra were obtained with 50 scans, resolution of 4 cm^{-1} in the range between 5000 and 400 cm^{-1}. A calibration curve was plotted using polyethylenes synthesized by metallocene/MAO catalyst whose $\langle M_n \rangle$ were determined with gel permeation chromatography analysis.

Results and discussion

The heterogeneous mesoporous-supported catalysts were prepared by treatment of the solids with methylaluminoxane prior to rac-$Me_2Si(Ind)_2ZrCl_2$ impregnation and their Zr content were near the same, around 0.05 mmol/g support. Table 1 shows the activities of homogeneous and supported catalyst systems in ethylene polymerization using different cocatalysts. Fouling in the reactor walls was not observed with the use of all the heterogeneous systems as detected in the homogeneous one with both cocatalysts.

The results show that, although the performance of the supported catalysts were lower than that of the homogeneous metallocene, the systems supported on SBA-15 and TiO_2 were more active for ethylene polymerization when the mixture MAO/TIBA was employed as cocatalyst in the reaction medium, in comparison with the performance

Table 1: Activities of the homogeneous and supported catalysts in ethylene polymerization

Catalyst	Cocatalyst [Al]/[Zr]	Catalyst Activity (kg PE/mol Zr*h).10^{-3}
Homogeneous Metallocene	MAO 1000	4.43
	MAO 100/TIBA 500	3.02
MCM-41/MAO/Metallocene	MAO 1000	0.38
	MAO 100/TIBA 500	0.36
TiO_2/MAO/Metallocene	MAO 1000	0.38
	MAO 100/TIBA 500	0.86
SBA-15/MAO/Metallocene	MAO 1000	0.93
	MAO 100/TIBA 500	1.05

Solvent – toluene 100 mL; [Zr]=50μM (rac-$Me_2Si(Ind)_2ZrCl_2$); T=60ºC; P_{Et}=2 bar; t=1h.

using the cocatalyst MAO. On the other hand, the use of less MAO cocatalyst in the polymerization using the homogeneous system has decreased its catalyst activity.

Especially the catalyst supported on mesoporous titanium oxide has increased its activity more than twofold in relation to the use of MAO as cocatalyst. In the case of MCM-41/MAO/Metallocene, the performance was as low as with the mesoporous TiO_2 system adding MAO in the reaction medium and did not vary with the type of cocatalyst.

It is believed that the highest activity observed for the catalyst SBA-15 /MAO /Metallocene with respect to the other heterogeneous systems could be related to the presence of isolated silanol groups (absorption band at 3700 cm^{-1}) in the support structure, as it is shown in the FTIR spectrum of SBA-15 support before MAO pre-treatment (Figure 1a). Moreover, the almost absence of associated OH groups (absorption band at 3400 cm^{-1}) could be also responsible for the high performance of this catalyst. The fixation of MAO on these associated groups could leave some unreacted hydroxyl (Figure 2) which would partially deactivate the metallocene species on the support surface during its impregnation.

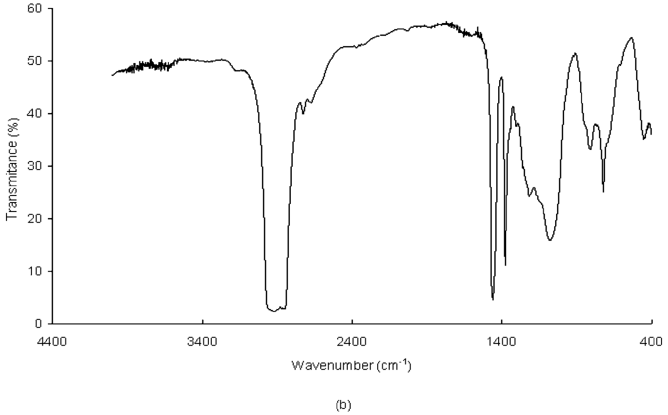

Figure 1a: FTIR spectra of mesoporous SBA-15 after thermal treatment (Nujol suspension)

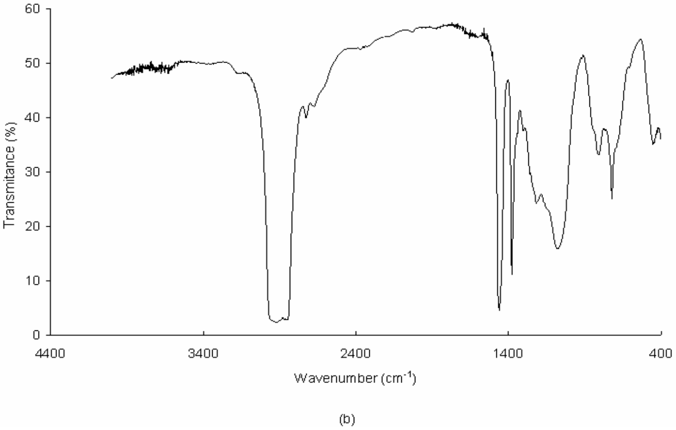

Figure 1b: FTIR spectra of SBA-15/MAO/Metallocene supported catalyst (Nujol suspension)

After the chemical treatment of SBA-15, the disappearance of the absorption band at 3700 cm^{-1} is noticed, as presented in Figure 1b, indicating that hydroxyl groups reacted with MAO added in the support pretreatment, leaving the support substantially free of OH groups, and assuring the formation of a higher number of active sites when the metallocene was added and, consequently, increasing the activity of that catalyst in relation to the others.

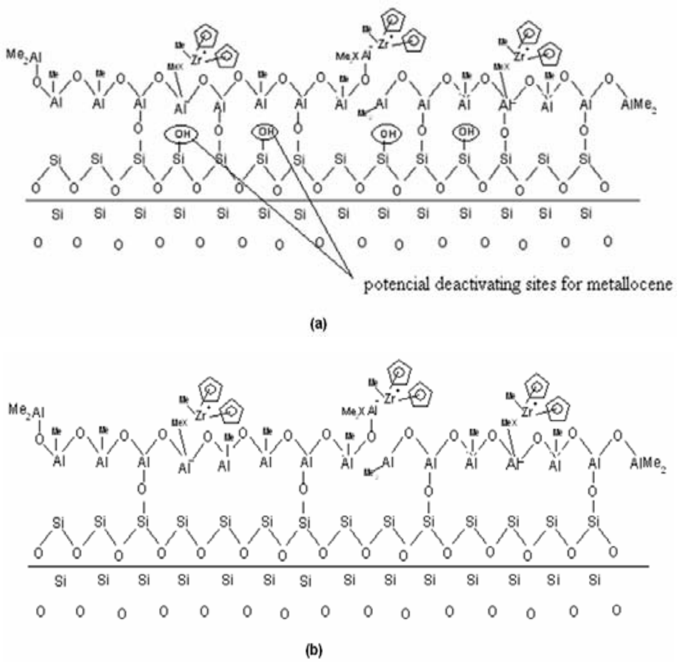

Figure 2: Model for the reaction of MAO and metallocene on the supports surface. (a) through associated –OH groups on general supports; (b) on isolated supports –OH groups as in the case of SBA-15

The catalyst system supported on MCM-41 presented lower activities than that of the catalyst supported on SBA-15. It is possible that the small OH contents on the surface of this material (Figure 3) were the responsible for the low activity of this catalyst. The low contents of hydroxyl species for the chemical adsorption resulted preferentially in the physical adsorption of MAO on this support. Due to the weak interaction in the physical adsorption, MAO probably suffered leaching during the washing processes in the catalyst preparation, leaving silanol groups, which has deactivated the metallocene complex during its impregnation.

In SBA-15, the presence of high amounts of free silanol groups on the surface of this material was decisive to achieve high performance in the polymerization of ethylene.

As for the catalyst system supported on mesoporous titanium oxide, the increase of activity when the mixture MAO/TIBA activates the system was a remarkable result, since this material do not possesses OH groups for the fixation of methylaluminoxane. The means that MAO reacts with this support surface is not known yet.

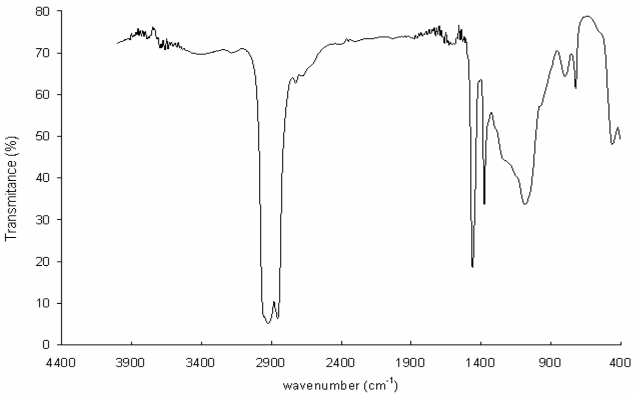

Figure 3: FTIR spectrum of mesoporous MCM-41 after thermal treatment (Nujol suspension)

The FTIR spectra of the mesoporous TiO_2 support in Nujol suspension or even of the supported catalyst did not reveal any chemical modification that could have happened in its surface, as expected. Besides, the zirconocene concentration on catalyst surface is very low (< 0.5% p/p), which difficult its analysis by other techniques.

Table 2 shows the main characteristics of the obtained polyethylene using the prepared catalyst systems.

Table 2: Characteristics of polyethylene obtained by rac-$Me_2Si(Ind)_2ZrCl_2$ homogeneous and supported mesoporous materials with different cocatalysts

Catalyst	Cocatalyst [Al]/[Zr]	T_m (°C)	X_c (%)	$^a\langle M_n\rangle * 10^{-5}$ (g/mol)
Homogeneous Metallocene	MAO 1000	134	64	1.12
	MAO 100/TIBA 500	130	45	0.78
MCM-41/MAO/Metallocene	MAO 1000	134	53	0.79
	MAO 100/TIBA 500	136	59	0.79
TiO_2/MAO/Metallocene	MAO 1000	130	48	0.73
	MAO 100/TIBA 500	135	60	1.01
SBA-15/MAO/Metallocene	MAO 1000	132	50	0.77
	MAO 100/TIBA 500	136	56	0.78

Solvent – toluene 100 mL; [Zr]=50µM; T=60ºC; P=2 bar; t=1h; ^{a} $\langle M_n\rangle$ obtained through FTIR (C=C end groups)

It can be observed that the polyethylene synthesized with the homogeneous metallocene catalyst rac-$Me_2Si(Ind)_2ZrCl_2$ cocatalyzed by the mixture MAO/TIBA have lower melting temperature (T_m) and crystalline degree (X_c) in comparison to the polymer obtained with MAO. This indicates that the produced polyethylene is more branched, probably because the metallocene counterion derived from MAO/TIBA is larger than MAO^-, separating the homogeneous ionic par $Zr^+/MMAO^-$ and allowing the incorporation in the polyethylene chain of unsaturated macromers (short chain branching) formed during the polymerization by β-hydrogen transfer reactions [12].

Besides, the ethylene-macromer copolymerization could also be responsible for the decrease in the catalyst activity of this system.

Moreover, the larger separation of the ionic active site also allows the higher frequency of chain transfer reactions, leading to a decrease in polymer molecular weight. Indeed, polymers obtained with MAO/TIBA as cocatalyst have lower $<M_n>$ than those with MAO, as indicated in Table 2. However, even though there is an error in this method for determining $<M_n>$ because the contribution of chain transfer to aluminum was completely neglect, this error is not very high since spontaneous β-hydrogen transfer reactions are more probable to occur in this polymerization system than chain transfer to aluminum.

On the contrary, the polymers synthesized with the catalysts supported on the mesoporous materials where MAO/TIBA was used possess increased T_m and X_c in relation to those obtained using only MAO as cocatalyst, indicating that the former polyethylenes are less branched. This behavior shows the influence of the supports and their steric hindrance, which difficult the incorporation of macromers. However, use of a larger cocatalyst as in the case of MAO/TIBA was beneficial for the catalyst activity. Moreover, the quite accentuated decrease of the crystalline degree in relation to the homogeneous system was observed in the polyethylene obtained with the catalyst system supported on TiO_2 cocatalyzed by MAO.

Concerning the results of the polymer molecular weight, a decrease was observed in the polymers obtained with the supported catalysts in comparison with that synthesized with the homogenous system. Only the polyethylene obtained with the TiO_2 supported catalyst cocatalyzed by the mixture MAO100/TIBA 600 has $<M_n>$ as high as that of the homogeneous polymer.

Conclusion

Metallocene catalysts rac-$Me_2Si(Ind)_2ZrCl_2$ supported on MCM-41, SBA-15 and TiO_2 mesoporous materials showed distinct behavior in comparison with the homogeneous corresponding system in the polymerization of ethylene. The most active supported catalyst was that using SBA-15 as carrier, followed by mesoporous TiO_2.

The most effective cocatalyst for the supported systems was the mixture MAO/TIBA as an alternative of MAO. Polyethylenes obtained with the mesoporous supported catalysts and MAO/TIBA have higher melting temperature and crystalline degree. Moreover, the supported catalysts in general resulted in polymers with lower molecular weights than the homogenous product.

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