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

João M. Campos [a], M. Rosário Ribeiro [a,*], João Paulo Lourenço [b], Auguste Fernandes [c]

[a] Instituto de Ciência e Engenharia de Materiais e Superfícies, Departamento de Engenharia Química e Biológica, Instituto Superior Técnico, Universidade Técnica de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
[b] Centro de Investigação em Química do Algarve, Departamento de Química, Bioquímica e Farmácia, Faculdade de Ciências e Tecnologia, Universidade do Algarve, Campus de Gambelas, 8005-139 Faro, Portugal
[c] Instituto de Biotecnologia e Bioengenharia, Departamento de Engenharia Química e Biológica, Instituto Superior Técnico, Universidade Técnica de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

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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.

Keywords: MCM-41; Zirconocene; Supported catalyst; Ethylene polymerisation; Nanofibres

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.

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[*] Corresponding author. Tel.: +351 218417325; fax: +351 218419198.
E-mail address: rosario@ist.utl.pt (M.R. Ribeiro).

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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 $dm^3/(g\,h)$), 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