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SILICA COATINGS AS METALLOCENE SUPPORTS: EFFECTS ON CATALYTIC ACTIVITY, DEGREE OF COMONOMER INCORPORATION AND PROPERTIES OF THE POLYMERS OBTAINED



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Most research on metallocenes has centered on homogeneous systems. Huge progress was achieved in the stereoselective polymerization of a wide variety of monomers. However, similar to the evolution of Ziegler-Natta catalysts, in recent years a large number of studies have been devoted to the transformation of soluble metallocene complexes on heterogeneous catalysts, supporting them on organic and inorganic materials. A large part of the efforts have gone into the study of both the nature of the support and the technique used to fix the metallocene on a metal oxide surface. These parameters have a crucial influence on the results of the catalytic behavior. The main supports consist of inorganic oxides such as silica, alumina and magnesium compounds, finely divided polymers and other materials with large surface area. Less common materials such as cyclodextrins,¹ polystyrene,² polysiloxane derivatives³ and zeolites⁴ have also been investigated.

Direct impregnation of the metallocene complex on the support was one of the first routes for the preparation of heterogeneous catalysts. Mixing temperature and contact time are important parameters which affect the catalytic yield and the properties of the polymer formed.^{5,6} In most cases, however, the behavior of the catalysts was deficient, achieving in ethylene polymerization reactions productivities of the order of 100 kgPE/(molMxh), (M = metal) and molecular weights close to 400.000 g/mol.⁷

A modification of the support can also be applied to improve the catalyst yield. This alternative may include reactions of the support with organometallic compounds (like alkylmagnesium or alkylaluminum) or other compounds such as SiCl₄, SiMe₂Cl₂, etc. Also, some researchers have recently reported the immobilization of these complexes on

silica by introducing spacing groups such as polysiloxane between the support and the metallocene.⁸ On the other hand, a prior reaction of a silica with methylaluminoxane (MAO) followed by the reaction of this modified support with a metallocene complex, resulted in a more active heterogeneous catalyst for olefin polymerization.⁹ This procedure is actually widely used to prepare supports for this type of catalyst, and it has been found to improve the catalytic activity of systems like SiO₂/MAO/Cp₂ZrCl₂/MAO in the polymerization reactions of ethylene, propene and other α -olefins.¹⁰

When the surface of the silica has been treated with MAO, the reaction with the metallocene complex may give rise to the formation of an ion pair such that the zirconocene (Zr⁺) species is semi-immobilized on the surface of the silica. As long as the ion interaction is weak, however, the zirconocene species may be able to migrate on the superficial layer of the support, and in this way the behavior of the catalyst may depend on this phenomenon (ion pair interaction). Also, the formation of more than one type of site or active species may depend on the MAO content on the surface of the silica and on the electronic exchange toward the aluminium atom.¹¹

This paper will show the results of the synthesis and characterization of silica based supports coated with oxides (TiO₂, MgO and mixed) via the sol-gel technique. It is expected to relate the characteristics of the support, the nature of the interaction with the metallocene complexes, and the effect of the latter on the catalytic behavior of the polymerization reaction of ethylene and its copolymerization with 1-octadecene with the polymer characteristics.

The modification by means of the sol-gel technique of the surface of the silica (ES70), with

inorganic oxides of the TiO₂, MgO, Al₂O₃ type and mixtures of these oxides is carried out with the purpose of achieving changes in the chemical reactivity of the surface of the ES70 silica. This is due to the presence of new components such as TiO₂ which are part of the SiO₂ matrix, so that the reaction of these new supports with MAO and a metallocene complex will affect positively the formation of a heterogeneous catalyst, making them more efficient in olefin polymerization reactions.

The results of the characterization by XPS, ISS, Zeta Potential, IR and ICP show that the coating of silica particles is possible by the sol-gel technique. The elemental composition (Al and Ti content) of the coated supports shows the presence of new components on the surface of the silica. For particles having a high specific area and pores, only a partial coverage of the surface is achieved. These results suggest that part of the surface of the silica is not accessible to the oligomers contained in the respective sols, probably because of their large size. On the other hand, after the coating by the sol gel, no changes in the morphology of the silica associated with particle breakage were observed.

The reaction of the supports modified with MAO via sol-gel, occurs on the superficial OH and M-O-Si groups (where M = may be Ti, Mg or Al) of these materials. The heterogenization of metallocene complexes on these supports, which contain 50% less superficial MAO in relation to supports widely reported in the literature, leads to highly active catalysts for the polymerization of ethylene (Table 1). This effect is associated with the characteristics of the coating.

Table 1.- Catalytic activity of the metallocene catalyst EtInd₂ZrCl₂(1) heterogenized on different modified supports.^(a)

Nº	Catalyst	% Zr	mol Zr x10 ⁶	Al/Zr	[g]	Activity [Kg/molZrxh*bar]
1	ES70M-1	0,12	5,8	1300	14	2300
2	SIO2M-1*	0,19	6,1	2500	16	2700
3	ES70MgM-1	0,15	4,1	3600	16	3900
4	ES70TiM-1	0,22	6,0	2500	22	3600
5	S1M-1	0,12	5,8	2600	23	3900

(a) Polymerization conditions: Reactor Büchi, 1 liter; Toluene = 500mL; Temperature = 60 °C; Pressure = 2 bar; Stirring speed = 1000 rpm; Reaction time =30 min.

* Witco commercial catalyst

The polymers obtained with the EtInd₂ZrCl₂ catalyst heterogenized on these supports are characterized by having an apparent density 4 times higher than that of the polymers obtained in a homogeneous phase. Additionally, the morphology of the polymer can be controlled by replicating the shape of the support particles. In ethylene polymerization

reactions in the presence of 1-octadecene, the comonomer is incorporated in the polymer chain (Table 2). The effects on the catalytic activity, the incorporated comonomer content, and the melting temperature of the polymer, are similar to the corresponding ones obtained in the homogeneous system.

Table 2.- Copolymerization of Ethylene with 1-Octadecene with catalyst EtInd₂ZrCl₂(1) heterogenized on different modified supports.^(a)

Catalyst	mol Zr x10 ⁶	Al/Zr	[g]	Activity [Kg/molZrxh*bar]	%- mol	η [dL/g]
SiO ₂ M-1*	2,76	2004	26,7	9700	1,3	1,4
ES70Ti5M-1	3,73	1200	40,6	10900	1,2	1,4
ES70MgM-1	3,91	1300	32,3	10100	1,4	1,4

(a) Polymerization conditions: Reactor Büchi, 1 liter; Toluene = 500mL; Temperature = 60 °C; Pressure = 2 bar; Stirring speed = 1000 rpm; Reaction time =30 min. [1-Octadecene]= 0.14 mol/L.

* Witco commercial catalyst

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