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The effects of partial replacement of $TiCl_4$ by $Ti(OR)_4$ on the performance of $MgCl_2$-supported Ziegler–Natta catalysts

Cristóvão de Lemos [a], Fernando Franceschini [a], Claudio Radtke [b], João H.Z. dos Santos [b,*], Carlos R. Wolf [c]

[a] Braskem S.A., BR 386 Rod. Tabaí-Canoas km 419 Via Oeste Lote 5, Passo Raso, 95853-000, Triunfo, Brazil
[b] Universidade Federal do Rio Grande do Sul, Instituto de Química, Av. Bento Gonçalves, 9500, 91501-970, Porto Alegre, Brazil
[c] Universidade Luterana do Brasil, Faculdade de Química, Av. Farroupilha, 8001, 92425-900, Canoas, Brazil

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ABSTRACT

In a Ti-based Ziegler–Natta catalyst with in situ generated $MgCl_2$, the titanium tetrachloride ($TiCl_4$) was partially replaced by titanium tetra-alkoxide ($Ti(OR_4)$), where R was either ethyl or n-butyl, and the effect of the addition order of the titanium compound was evaluated. For comparison, two other catalysts were synthesized: (1) one had the same amount of Ti, exclusively from $TiCl_4$; (2) the other is employed in industrial processes and was used as the reference. Ti^{3+} comprised 85% of the total amount of titanium added during the catalyst synthesis. The amount of soluble Ti in the supernatant phase was at most 0.002 mol L^{-1}, indicating that the added Ti reacted with the support. In general, Ziegler–Natta catalysts demand a significant amount of raw materials, while these catalysts require a lower amount of titanium compounds and save a significant amount of solvent in particular during the synthesis (approximately 80%). The preparation time of the catalysts was also reduced. The performance of these catalysts during ethylene polymerization suggests that adding $Ti(OR)_4$ created a catalyst with a similar activity and ability to form high-density polyethylene as the reference catalyst.

1. Introduction

Although Ziegler–Natta (ZN) catalysts were first discovered in 1953, these polymerization catalysts are still the subject of ongoing research. Recent literature has examined various aspects of these catalysts, such as the control of titanium oxidation state [1], the effect of external or internal donors [2,3], the effect of the co-catalyst [4], the effect of the support [5], the development of new catalysts [6], and the kinetics and modeling studies [7,8] of the catalysts, among others. In addition to the catalyst architecture, the polymerization conditions and industrial processing also play fundamental roles in producing polymers with a variety of properties, motivating the ongoing research efforts for these systems [9–14].

In the 1980s and 1990s, Hoechst presented a series of patents that described preparation method for ZN catalysts, which generated huge industrial interest [15,16]. The recommended magnesium alkoxide is magnesium ethoxide, $Mg(OC_2H_5)_2$, whose particle size significant affects the melt flow rate (MFR) of the resulting polymers. This property affects the processability or flow of the polymer under a specific shear rate and temperature and can be correlated with the particle size of $Mg(OC_2H_5)_2$ [17–20]. The incorporation of titanium tetra-ethoxide ($Ti(OC_2H_5)_4$) after the reaction between $Mg(OC_2H_5)_2$ and $TiCl_4$ contributes to the satisfactory catalytic activity, apparent density, and medium particle size (d_{50}) when compared to the reference catalyst ($TiCl_4$) and to the PE produced in industrial processes [21]. Furthermore, catalyst preparation requires a hydrocarbon solvent to remove by-products between the two reaction steps.

Other studies partially replaced $TiCl_4$ with titanium alkoxide, $Ti(OR)_4$, which presents at least one alkoxide ligand attached to titanium. Titanium tetra-alkoxides are extensively used in catalysts to polymerize olefin compounds [22–28]. In the 1980s, Solvay used a ZN catalyst to polymerize ethylene, creating PE with a high impact resistance. The ZN catalysts involve the reaction between $Mg(OC_2H_5)_2$ and titanium tetrabutoxide, $Ti(OC_4H_9)_4$, followed by the reaction with dichloride ethyl aluminum, $Al(C_2H_5)Cl_2$. Small amounts of $Ti(OC_4H_9)_4$ and $Al(C_2H_5)Cl_2$ (Al/Ti ratio of 50) increased the catalytic activity and the polymeric melt flow rate [29]. In 1993, Enichem Polimeri [30] patented a technique for polymerizing ethylene using a bi-supported catalyst in silica (SiO_2) and magnesium chloride ($MgCl_2$) using $TiCl_4$, $Ti(OC_4H_9)_4$ and ethyl aluminum sesquichloride, $Al_2(C_2H_5)_3Cl_3$ (EASC). The ethylene polymerization was carried out in a bench reactor for 90 min using hexane as the solvent, triethylaluminum (TEA) as the co-catalyst, and an Al/Ti ratio of 50 in the polymerization. The equimolar combination of the two sources of titanium produced PE with different properties and

* Corresponding author. Tel.: +55 51 3316 7238; fax: +55 51 3316 7304.
E-mail address: jhzds@iq.ufrgs.br (J.H.Z. dos Santos).

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