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Metallocenes and post-metallocenes immobilized on ionic liquid-modified silica as catalysts for polymerization of ethylene

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ABSTRACT

The supported ionic liquid (SIL) strategy was used for the first time to metallocene and post-metallocene heterogeneous catalysts for olefin polymerization. The metal complexes: Cp_2TiCl_2, Cp_2ZrCl_2, FI–Ti, and Sal–Ti were immobilized in the 1-(3-triethoxysilyl)propyl-3-methylimidazolium alkylchloroaluminate ionic liquid, anchored on the surface of the mesoporous amorphous silica. The SIL systems were characterized by FTIR, ^{29}Si NMR, N_2 adsorption, EA, AAS, TG, and SEM techniques. The developed supported catalytic systems were found to be active in the ethylene polymerization and produce the polyethylene of various properties.

1. Introduction

Polyethylene (PE) is the most common and important polyolefin polymer. It is characterized by good mechanical properties, chemical inertness, and low cost of productions [1,2]. Therefore, there is a continuous search of new organometallic catalysts for ethylene polymerization, which will have better activity or selectivity. Metallocene and post-metallocene catalysts attract a special attention because variation in their structure not only provides a possibility to control polyreaction performance but also enable to tailor polymer properties [3–7]. These catalysts are usually investigated as homogeneous systems, which show high activities in olefin polymerizations [8–10]. However, use of large amounts of solvents, lack of ability to control polymer microstructure and morphology, and undesirable phenomenon of reactor fouling are main disadvantages of the homogeneous catalysts [11–14]. For industrial applications, supported metallocenes and post-metallocenes are more appropriate because they can be used in gas- and slurry-phase processes. The polymer of uniform particles with narrow size distribution and high bulk density is produced and problems with the reactor fouling are prevented [15,16]. Amongst various supports of the organometallic catalysts, amorphous silica is the most widely used. This environmentally friendly support has good mechanical properties, stability and inertness under reaction and processing conditions, relatively large surface area and porosity. There is also possible to control the amount and distribution of hydroxyl groups on its surface [11,13,15,17–19]. Usually, the silica surface is modified with appropriate thermal treatment or chemical treatment by using dehydroxylating agent such as hexamethyldisilazine (HMDS) [20]. However, in ethylene polymerization using zirconocene catalyst, after HMDS-treatment, the catalyst shows lower activity and produces polymers of lower molecular weight and broader polydispersities, in comparison to the catalyst on non HMDS-treated silica. Another approach for immobilization of metallocene on silica support involves use of silane coupling agents, such as $Cp(CH_2)_3Si(OCH_2CH_3)_3$ [21,22]. The zirconocene catalysts supported on silica, chemically modified by $(CH_3)_3SiCl$ (TMCS), show a sufficiently high activity in ethylene polymerization (up to 1638 kg_{PE}/molZr h bar) [23], but obtained polyethylene consists of shapeless aggregates similar to those obtained with homogeneous catalysts [24]. Alonso et al. prepared a supported metallocene catalyst (Cp_2ZrCl_2) by chemical modification of silica by silicon ethers, $EtOSiMe_3$ and $(Me_3Si)_2O$, or a silazane, $(Me_3Si)_2NH$. The activity of these systems in polymerization ethylene was 441 and 620 kg_{PE}/molZ h, respectively for $Cp_2ZrCl_2/[SiO_2\text{-}EtOSiMe_3]$ and for $Cp_2ZrCl_2/[SiO_2\text{-}(SiMe_3)_2O]$. In the case of $Cp_2ZrCl_2/[SiO_2\text{-}(SiMe_3)_2NH]$ only traces of product were obtained [24].

The most common method to modify silica is to tread this support, first with alkylaluminium compound (mainly MAO or $AlMe_3$), and then to absorb metallocene on it. Janiak and Rieger reported that activity of the zirconocene catalyst supported on the methylalumoxane-pretreated SiO_2 was up to 4716 kg_{PE}/molZr h, but without modification by using MAO it did not exceed 70 kg_{PE}/molZr h [25]. Both nano- and micro-sized MAO-modified

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silica were used to support the Cp_2ZrCl_2 catalyst for ethylene polymerization [26]. The nano-sized catalyst exhibited much better activity in ethylene polymerization than micro-sized catalyst (3.8×10^4 and 8730 kg_{PE}/molZr h, respectively), which was attributed to the large specific external surface area, the absence of internal diffusion resistance, and the better active site dispersion for the nano-sized catalyst.

Despite of many advantages, application of silica modified by MAO or TMA as a support of metallocene catalyst requires use of toluene as solvent and additional amount of MAO as catalyst activator. Moreover, it is observed unfavorable effect of leaching catalyst from silica surface [14,27–30].

Recently, there has been an interest in immobilization of ionic liquids (ILs), on the surface of a support, usually silica, so-called supported ionic liquid (SIL) concept [31–33]. Ionic liquids, due to their negligible vapour pressure, large liquid range, and high thermal stability gain increasing attention and they are considered as useful solvents with multiple applications in synthesis and catalysis [34–42]. In most cases the ionic liquids are applied in homogeneous or biphasic systems, which reveal a great potential in laboratory scale, but seem do not show a significant promise for large-scale industrial catalytic applications [43]. In these systems, large quantities of the ILs are used as solvents or catalysts, which inevitably generate lots of waste materials. Their disposal is extremely difficult and makes the overall process unacceptable from environmental and economic viewpoint. Application of the SIL systems enables to avoid such obstacles [31,32,44,45]. These systems offer a very efficient ionic liquid utilization, provide relatively short diffusion distances of reactants as compared to the biphasic catalyst systems organic liquid – ionic liquid, and thus solve problems of mass transport limitation [32,45–47]. Moreover, this type of the catalyst systems can be tuned by optimizing structures of the IL, transition-metal catalyst, and solid support. The ILs immobilized on various supports were successfully checked in many catalytic reactions, for example, in hydroformylation [48], alkylation [49], epoxidation [50], hydrogenation [51]. So far, there is no literature data regarding applications of the SIL strategy for development of a heterogeneous catalytic system for polymerization of olefin. In this work, we report application of the SIL system with metallocene and post-metallocene catalysts in ethylene polymerization. The influence of the kind of catalyst used, and applied reaction conditions on the performance of the polymerization as well as the on properties of the obtained polyethylene is also presented.

2. Experimental

2.1. Preparation of the SIL system

All experimental steps have to be carried out under an inert atmosphere. The amorphous silica (3 g, 0.05 mol) was calcined for 4 h at 500 °C and stored under argon. Calcined silica was transferred to a round bottom flask and 1-(3-triethoxysilyl)propyl-3-methylimidazolium chloride (5.0×10^{-3} mol) in toluene (80 cm^3) was added. The mixture was stirred at 80–90 °C for 18 h. In the next step, solvent and ethanol created in the grafting step were distilled off. The remaining solid in form of powder was dried under vacuum, washed with hexane (5× 30 cm^3) in a Schlenk apparatus, dried under vacuum, then extracted for 24 h with boiling dichloromethane in an Soxhlet apparatus, and dried under vacuum. Such obtained solid was then added to a solution of $AlCl_3$ (2.0×10^{-3} mol) in toluene (50 cm^3), and left stirring for 1.5 h at room temperature. After filtration in the Schlenk apparatus the support was washed hexane (4× 30 cm^3), dried under vacuum, extracted for 20 h with boiling dichloromethane in the Soxhlet apparatus, and dried under reduced pressure. The solid was mixed with $AlEtCl_2$ (2×10^{-4} mol) in hexane (60 cm^3) in a ball mill for 2 h. The obtained support was filtered in Schlenk apparatus, washed hexane (4× 30 cm^3) and dried under reduced pressure.

Table 1
Characteristics of the catalytic systems.

Catalytic system	Support	Catalyst precursor
A	SIL	Cp_2TiCl_2
B	$SiO_2/AlEtCl_2$	Cp_2TiCl_2
C	SIL	Cp_2ZrCl_2
D	SIL	FI–Ti
E	SIL	Sal–Ti

SIL: SiO_2/IL-Cl/$AlCl_3$/$AlEtCl_2$; Fi–Ti: bis[*N*-(salicylideno)anilinato]-titanium(IV) dichloride; Sal–Ti: *N,N′*-ethylenebis[5-chloro-salicylideneiminato]titanium(IV) dichloride.

2.2. Immobilization of catalysts on the ionic liquid-modified silica support

All experimental steps were performed in inert atmosphere. The prepared support (1 g) was mixed with catalyst precursor (2.5×10^{-5} mol Mt) dissolved in deoxygenated toluene (5 cm^3) and hexane (50 cm^3) in a ball mill for 24 h. The obtained catalyst system was filtered in Schlenk apparatus, washed hexane (4× 20 cm^3), and dried under nitrogen stream. The Cp_2TiCl_2 precursor mixed with the support gave the catalytic systems denoted as A. Analogously, the precursors Cp_2ZrCl_2, FI–Ti, and Sal–Ti were mixed with the support in order to obtain respectively the catalytic systems C, D, and E (Table 1). The obtained catalytic systems were in the form of powder, slightly yellow for Ti systems and off-white for Zr system. For comparison, the catalyst system B was prepared (Table 1), in which the titanocene catalyst (Cp_2TiCl_2) was immobilized without IL, directly on silica calcinated in 500 °C, and modified only by $AlEtCl_2$ (molar ratio $SiO_2/AlEtCl_2 = 10/1$).

2.3. Polymerization of ethylene

To a glass reactor (500 cm^3) filled with inert nitrogen atmosphere, hexane (150 cm^3), $AlEt_2Cl$ or $AlEtCl_2$ or MAO ($1.0–6.0 \times 10^{-3}$ mol) and the supported catalytic system (2.0×10^{-6} mol Ti or Zr) were added. The ethylene was introduced at 0.5 MPa and the polymerization reaction was carried out at 30 °C or 50 °C for 30–90 min. The reaction was quenched by closure of the ethylene feeding, reduction of the pressure to 0.1 MPa, and addition of acidified methanol to the reaction mixture. The polyethylene product was filtered, washed thoroughly with methanol, dried at room temperature, and then stored for subsequent characterization.

2.4. Leaching experiment for SIL catalytic system

Hexane (150 cm^3), $AlEt_2Cl$ or $AlEtCl_2$ or MAO (4.0×10^{-3} mol), and the supported catalytic system (2.0×10^{-6} mol Ti or Zr) were added in inert atmosphere to glass flask equipped with mechanical stirrer and heating jacket. The mixture was mixed vigorously at 30 °C or 50 °C for 30 min. Maintaining inert atmosphere, the solid was filtered and hexane phase was placed into reactor where it was taken into the ethylene flush at typical polymerization conditions (0.5 MPa, 30 °C or 50 °C, 30 min.). The solution was transparent and no polyethylene was obtained. The absence of Ti or Zr in the hexane phase was also confirmed by atomic absorption spectrometry (AAS).