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Heterogeneous catalyst mixtures for the polymerization of ethylene

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Abstract

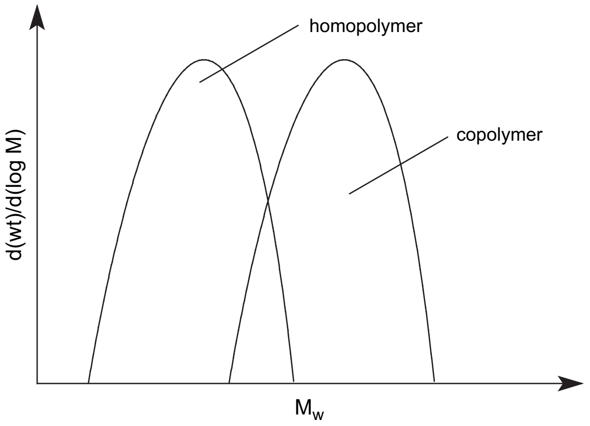
Heterogeneous cocatalysts, catalysts, and catalyst mixtures for the polymerization of ethylene were prepared applying "fumed silica" and mesoporous MCM-41 support materials and zirconocene dichloride, titanocene dichloride, and a bis(arylimino)pyridine iron complex as catalyst precursors. The catalyst mixtures produced polyethylenes which exhibit the properties of two single polymers. Polyethylenes with the desired bimodal molecular weight distributions could be obtained with a series of ternary Zr/Ti/Fe catalysts. The ability of the zirconium and titanium species to copolymerize short-chain 1-olefins produced by the iron centers ("in situ" copolymerization) is useful for the production of copolymers from only one monomer (ethylene).

Keywords: Heterogeneous catalysts; Ethylene polymerization; Polyethylene

1. Introduction

During the past 25 years, metallocene complexes have been extensively studied as catalysts for the homogeneous and heterogeneous polymerization of α-olefins ([1–26] and references therein). The produced polyolefins have narrow molecular weight distributions due to identical active sites of the catalyst. However, this can be disadvantageous for industrial processings like extrusion or injection moulding. Therefore, a huge number of inorganic and organic compounds have been tested as support materials for catalyst precursors for the heterogeneous polymerization of 1-olefins. Silica gels are the most common supports [27–32], but many other materials like magnesium chloride [33–36], aluminum oxide [37–39], charcoal [40], polypropylene [41], polystyrene [42,43], zeolites [44–48], μ-gels [49–58], starch [59], or even cherry pits [60] were applied. Due to their high surface areas, zeolites, especially mesoporous crystalline materials (e.g. MCM-41), have attracted a lot of attention as support materials in the past few years.

Besides broader molecular weight distributions, regularly distributed branches at the polymer chains can also improve the mechanical properties of polyolefins. Such "linear low density polyethylenes" (LLDPEs) are obtained by copolymerization of ethylene with short-chain 1-olefins. An ideal polyolefin would consist of a low molecular weight homopolymer and a high molecular weight 1-octene/ethylene copolymer (Scheme 1).



Scheme 1. Desired molecular weight distribution of polyolefins for technical processing.

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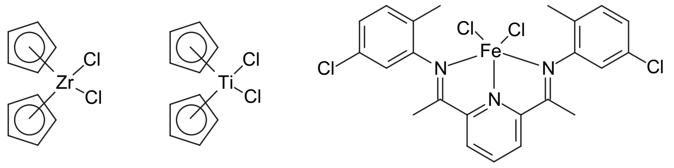
In order to obtain broader molecular weight distributions, cumbersome or costly approaches, like the blending of different resins, are necessary. On the other side, in most cases, it is not possible to obtain the desired multimodal resins by mixing individual mononuclear catalysts (averaging effect). Dinuclear complexes [61–66] proved to be useful catalyst precursors for the synthesis of such materials but their time-consuming synthesis and possible interactions between the active centers made us look for an easier access to polyolefins with the desired properties. A better separation of the active centers of polymerization catalysts may be achieved with heterogeneous catalyst mixtures. Therefore, mononuclear catalyst precursors were activated with heterogeneous cocatalysts. Varying the amount and the type of the applied catalyst precursors, polymers with modified properties should be obtained. Employing precatalysts that are able to copolymerize ethylene with higher 1-olefins, copolymers would be produced "in situ".

2. Results and discussion

2.1. General remarks

As catalyst precursors, zirconocene dichloride (**I**), titanocene dichloride (**II**), and bis(arylimino)pyridine iron complex (**III**) [67] (Scheme 2) were employed.

While the metallocene complexes **I** and **II** produce polyethylenes with different molecular weights, the iron complex **III** was applied to oligomerize ethylene to give 1-olefins like 1-octene. These oligomers would be consumed by the metallocene complexes producing an ethylene/1-olefin copolymer.



I **II** **III**

Scheme 2. Selected catalyst precursors: zirconocene dichloride (**I**), titanocene dichloride (**II**), bis(arylimino)pyridine iron dichloride complex (**III**).

Due to their high surface areas, zeolites, especially mesoporous crystalline materials (e.g. MCM-41), have been chosen as support materials. These zeolites exhibit crystalline structures and were first described in 1992 by Mobil Research and Development Corporation [68]. Advantageous are their high surface areas (>1000 m^2/g) and uniform hexagonal pores. The pore diameters can be adjusted to 20–100 Å by varying the reaction conditions. Inside and outside the pores, these compounds contain free hydroxyl groups. Depending on the reaction conditions, materials with higher (hs MCM-41) or lower (ls MCM-41) surface areas can be prepared by template synthesis. The surface area of hs MCM-41 was determined to ~1090 m^2/g while a pore diameter of 34 Å and a pore volume of 0.45 ml/g were found. The surface area of ls MCM-41 was determined as 500 m^2/g.

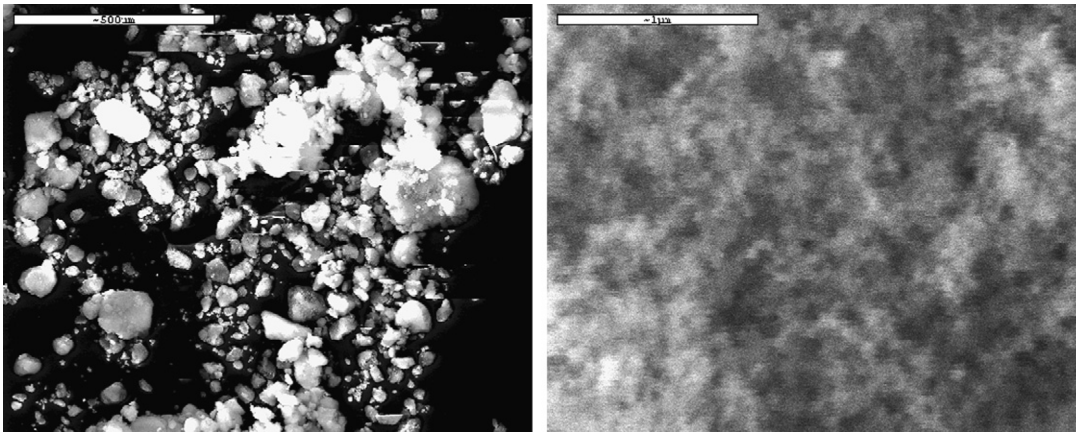
Besides MCM-41, "fumed silica" (Sigma Aldrich, $a = 200\ m^2/g$) and Davison-SiO_2 (Davison 948, calcined) were employed for the synthesis of heterogeneous catalysts. The support materials were characterized by SEM and EDX revealing that "fumed silica" is an amorphous silica gel and consists of irregularly formed particles which can be described as agglomerates of smaller particles with sizes below 50 nm (see Scheme 3).

SEM photographs of hs MCM-41 showed chunkier spherical particles and smaller irregularly formed motes (Scheme 4). At higher resolution, a mixture of differently formed small particles and particles with "worm-like" structures were observed.

Silicon atoms in MCM-41 can be partially substituted with tetravalent metals like titanium (TiMCM-41) or zirconium (ZrMCM-41) applying $Ti(OBu)_4$ or $Zr(OBu)_4$ as starting materials.

2.2. Synthesis and characterization of the heterogeneous cocatalysts

The heterogeneous cocatalysts were prepared by the "PHT method" [54–57]. Trimethylaluminum is added to a suspension of the support material in toluene. After careful addition of a defined amount of water steam (usually H_2O:Al ~ 1:1), partially hydrolyzed trimethylaluminum (PHT) is obtained on the surface of the support material. In contrast to



Scheme 3. SEM photographs of "fumed silica". Left: scale 500 µm; right: scale 1 µm.