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# *In situ* copolymerization of ethylene to linear low-density polyethylene (LLDPE) with calcosilicate (CAS-1) supported dual-functional catalytic system

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## Abstract

Calcosilicate (CAS-1) was used for the first time as an effective carrier for simultaneous immobilization of a dual-functional catalytic system consisted of iron-based bis(imino) pyridyl complex (**O**) and zirconocene compound (**C**) to form heterogeneous catalyst precursor (CAS-1/**O**/**C**). The α-olefins formed form **O**-catalyzed ethylene oligomerization copolymerized *in situ* with ethylene to linear low-density polyethylene (LLDPE) under the catalysis of **C** in CAS-1/**O**/**C** upon addition of cocatalysts as described hereafter. Instead of methylaluminoxane (MAO), triethylaluminum (TEA) was employed to activate the copolymerization reaction with high catalytic activities and smooth kinetic process. Experimental results reflected that the selectivity for lower α-olefins was improved due to the confinement effect of the layered structures of CAS-1, hence greatly increasing the incorporation rate of α-olefins into LLDPE main chains and the branching degree accordingly during the *in situ* copolymerization of α-olefins and ethylene. The layered structure of CAS-1 endowed the resultant LLDPE with improved thermal stability in addition to higher molecular weights ($M_n$).

*Keywords:* *In situ* copolymerization; Ethylene; CAS-1; Support; Dual-functional catalyst

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## 1. Introduction

Synthesis of linear low-density polyethylene (LLDPE) through *in situ* copolymerization of ethylene is an important and rapidly developing methodology in the field of polyethylene (PE) production. In 1984 this concept appeared first in academic field as tandem reaction in which α-olefins were *in situ* formed firstly from ethylene oligomerization catalyst and the as-synthesized α-olefins copolymerized with ethylene to LLDPE subsequently under the catalysis of organometallic compounds [1,2]. The advantage of this LLDPE preparation method is obvious due to the employment of a single monomer-ethylene feedstock and two catalysts in only one reactor. Based on the aforementioned original work various attempts concerning different combinations of ethylene oligomerization and copolymerization catalysts were performed subsequently [3–8]. However, drawbacks inherent in the reaction system of this type come forth such as interferences between the oligomerization catalyst and copolymerization catalyst, the dual-functional catalytic system and cocatalysts, and poor control over the selectivity for α-olefins and chain structure of the resulting LLDPE.

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With the development of late-transition metal catalysts possessing high ethylene oligomerization activity and selectivity for α-olefins hard nut to crack encountered with the above catalytic system is no longer insurmountable. The combination of iron-containing complex and zirconocene compound gave rise to structure-adjustable LLDPE with methylaluminoxane (MAO) the only cocatalyst [9–11]. Taking similar routes succeeding work also produced LLDPE under the catalysis of different dual-functional catalytic systems [12–15].

In order to make the present LLDPE production process accessible to industrial application issues standing in the breach like reactor fouling and implosion accompanied with the utilization of homogeneous dual-functional catalyst have to be tackled with great efforts. Heterogenization of homogeneous catalysts by immobilizing on supports such as silica, $MgCl_2$, and montmorillonite (MMT) [15,16] has proved to be effective examples in coping with the above disadvantages.

Found in our earlier research is that the introduction of MMT as the carrier to $(acac)_2ZrCl_2$ tripled the selectivity to 1-hexene in comparison to the homogeneous analogue mainly due to the confinement effect of the layered structures of MMT [16]. As known to many researchers the accessibility to facile adjustment of the selectivity to the α-olefins formed *in situ* is of vital significance in obtaining well-defined chain structures. To further tap the potential of catalyst carriers with layered structures CAS-1, a cacosilicate developed [17] and structurally confirmed [18] recently, is adopted herein to simultaneously support the dual-functional catalytic system. The objective of this art aims at good control over the selectivity for α-olefins of the oligomerization catalyst while maintaining its high catalytic activities. Meanwhile this methodology might give full play to the excellent copolymerization ability of zirconocene compound without excessive use of MAO introduced from out of the polymerization system. Also in expectation of the above-mentioned supported catalytic system is a smooth kinetic process and improved morphology of the resultant LLDPE.

## 2. Experimental

### 2.1. Materials

All manipulations of air- and/or moisture-sensitive compounds were carried out using drybox procedures or standard Schlenk techniques. 2,6-diacetylpyridine (97 wt%), 2,6-difluoroaniline, and *rac*-$Et(Ind)_2ZrCl_2$were from procured Acros (USA). Ethylene of polymerization grade was generously provided by Yanshan Petro-Chemical Ltd. Co. (China) and used without further purification. MAO solution in toluene (1.4 mol/L) was purchased from Albemarle Corp. (USA). Toluene, hexane and tetrahydrofuran (THF) were refluxed with sodium/benzophenone and freshly distilled prior to use. All other chemicals were obtained commercially and used without further treatment unless indicated otherwise.

### 2.2. Synthesis of CAS-1

CAS-1 was synthesized as the following: 2 g of $Ca(NO_3)_2 \cdot 4H_2O$ (⩾96 wt%, Beijing Hongxin Chemical Factory) was dissolved in 25 mL of distilled water. Then 10.43 mL of colloidal silica (6.05 mol/L aqueous solution, Qingdao Chemical Factory) was added to the solution. Finally, 2.41 g of KOH (⩾82 wt%, Beijing Chemical Factory) were added at room temperature and the mixture was stirred for 30 min more. The gel composition was $0.28K_2O:0.13CaO:1SiO_2:22H_2O$. This gel was transferred to a teflon-lined stainless steel autoclave, and the crystallization was carried out at 220 °C under autogenetic pressure without stirring for six days. The autoclave was then removed from the oven and cooled, and the product was separated by centrifuging, washed with distilled water six times and dried subsequently in air at 110 °C.

### 2.3. Synthesis of $\{[(2\text{-}ArN{=}C(Me))_2C_5H_3N]FeCl_2\}$ $(Ar = 2,6\text{-}F_2\text{–}C_6H_4)$ (***O***)

2,6-diacetylpyridine (0.5 g, 3.06 mmol), 2,6-difluoroaniline (0.92 g, 7.14 mmol), $MAO/SiO_2$ (0.31 g), and 4 A molecular sieve (1.04 g) were transferred to a round-bottom flask with desired amount of toluene and the reactants were stirred for 24 h at 35 °C. Removing the solids from the mixture and washing the organic phase with toluene repeatedly an oily yellow substance was obtained after the removal of most of the solvent under vacuum. The addition of cold methanol resulted in the formation of flaxen powders, which was confirmed to be the desired ligand after filtration and desiccation (yellow crystals 0.74 g; yield 62%) $\{[(2\text{-}ArN{=}C(Me))_2C_5H_3N]FeCl_2\}(Ar = 2,6\text{-}F_2\text{–}C_6H_4)$ was formed by addition of the ligand to $FeCl_2 \cdot 4H_2O$ in THF.

Ligand ($C_{21}H_{15}F_4N_3$) $^1H$ NMR ($CDCl_3$):$\delta = 8.47$(d, 2H, Py-*m*-H), 7.93(t, 1H, Py-*p*-H), 7.07(t, 4H, Aryl), 6.99(d, 2H, Aryl), 2.46(s, 6H, N=C–$CH_3$). EI: *m/z* 385[$M^+$]. Elemental analysis: Calc (%): C, 65.45;H, 3.92; N, 10.90; Found (%): C, 65.61; H, 4.02; N, 10.78. IR (KBr): 1636 (*ν*C=N), 1576, 1465, 1369, 1277, 1237, 1215, 1126, 1032, 1002, 827, 789, 759 $cm^{-1}$.

Complex ($\{2,6\text{-}(2,6\text{-}F_2C_6H_3N{=}CCH_3)_2C_5H_3N\}FeCl_2 \cdot H_2O$) Elemental analysis: Calc (%): C 47.58, H 3.23, N 7.92; Found (%): C 48.36, H 3.38, N 7.77.

### 2.4. Preparation of CAS-1-supported O (CAS-1/O)

CAS-1 (1.5 g) was dried at 150 °C in vacuum to constant weight and reacted with MAO at 50 °C for 15 h before washed with large amount of toluene to remove un-reacted MAO. Then, 62 μmol of **O** together with 15 mL of toluene were added and reacted at 50 °C for 8 h. The supported catalyst was washed several times with toluene until the