

Co-Supported Tandem Catalysts For Production Of Linear Low Density Polyethylene From An Ethylene-Only Feed

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Supporting Information

Content

A. Experimental	2
B. NMR spectra	4
C. Kinetic model	4
D. Polymer properties	6
E. References	7

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A. Experimental

General Considerations

All reactions unless otherwise stated were carried out under an inert dinitrogen atmosphere using standard glovebox, Schlenk line and high-vacuum line techniques. Toluene was obtained from a solvent purification system with activated alumina columns, degassed and left over 4 Å molecular sieves for at least 16 hours prior to use. Methylaluminoxane (MAO) (30% w/v in toluene) was obtained from Albermarle Corporation and stored at -30 °C in a dinitrogen glovebox freezer. Silica (MS-3030) was obtained from PQ Corporation at heated at 300 °C under vacuum for 5 h and then stored in a dinitrogen glovebox. (FI)TiCl₃ and (Cp*SiNR)TiCl₂ were prepared according to literature procedures.^{1,2} ¹³C labelled 1-hexene was synthesized from ¹³C labelled methyl iodide according to a literature procedure.³ Ethylene was purified by passage through a column containing activated molecular sieves and MnO dispersed on vermiculite.⁴ Polymerizations at pressures > 1atmosphere were carried out in a glass reactor (miniclave steel™ type 1 / 300 mL, 10 bar) obtained from Buchiglas-USA.

Representative procedure for the preparation of co-supported catalysts

In a dinitrogen-filled glovebox a 100 mL round bottom flask was charged with a Teflon stir bar, MS-3030 silica (2.000 g) and toluene (25 mL). 3.5 mL of 30 weight % MAO was added dropwise to this stirring suspension, and stirring at ambient temperature was continued for 2 hours, followed by addition of a mixture of (FI)TiCl₃ (8.2 mg, 14 μmol) and (Cp*SiNR)TiCl₂ (15 mg, 41 μmol) in toluene (10 mL). After inserting a 180° connector equipped with a Teflon valve the flask was taken out of the glovebox and attached to a vacuum line. The suspension was stirred at 30 °C for 1 hour, then toluene was removed under vacuum to obtain a dry yellow powder (yield: 2.971 g).

Representative procedure for tandem trimerization and copolymerization of ethylene at 1 atmosphere

In a dinitrogen-filled glovebox, a 250 mL round bottom flask was charged with a Teflon stir bar, s-(FI)Ti(1)-(Cp*SiNR)Ti(3) (0.302 g) and 50 mL of toluene. After inserting a 180° connector equipped with a Teflon valve the flask was moved from the glovebox to a vacuum line, and the slurry was cooled and degassed under high vacuum. Ethylene was supplied at 1 atm, and the reaction mixture was stirred for 3 hours at 25 °C, after which the reaction was quenched with 2 mL of 12 M HCl and 10 mL of methanol. Acetone (20 mL) was added to aid polymer precipitation; the solid was filtered off and washed with methanol. The isolated polymer (yield: 11.7 g) was dried under vacuum for 3 hours. Polymer samples for NMR analysis were prepared by the addition of ~20 mg of material to 1 mL of 1,1,2,2-tetrachloroethane-*d*₂. ¹³C{¹H} NMR spectra were obtained with a Varian 500 MHz spectrometer at 130 °C with a relaxation delay of 2 seconds.

Representative procedure for tandem trimerization and copolymerization of ethylene at pressures > 1 atmosphere

In a dinitrogen-filled glovebox, a miniclave steel™ glass reactor was with a Teflon stir bar, s-(FI)Ti(3)-(Cp*SiNR)Ti(1) (0.302 g) and 50 mL of toluene. The sealed reactor was removed from the glove box and ethylene was supplied at 4.4 bar. The reaction was stirred for 3 hours at 25 °C, after which the reaction was quenched with 2 mL of 12 M HCl and 10 mL of methanol.

Acetone (20 mL) was added to aid polymer precipitation; the solid was filtered off and washed with methanol. The isolated polymer (yield: 8.95 g) was dried under vacuum for 3 hours.

Tandem trimerization and copolymerization of ethylene with added 1-hexene

The procedure is similar to the above except for the addition of 1-hexene with a micro syringe after the addition of toluene. After inserting the 180° connector the reactor assembly was immediately removed from the glovebox and frozen (to reduce poly-1-hexene formation), prior to attaching it to the high vacuum line for degassing and the addition of ethylene.

Gel Permeation Chromatography

Chromatographic Conditions

HT-GPC

Solvent:	TCB (1,2,4-Trichlorobenzene)
Flow rate:	1.0 ml/min
Injection volume:	200µl
Column/ Detector temperature:	140 C°
Columns:	3x ViscoGEL HR-(S) HT 7.8cm

GPC System HT-GPC 350A

Sample Preparation for high temperature GPC

About 5.5 mg of the material was placed into a 40 ml glass vial and accurately weighed. 10ml of the solvent was added using a clean 10 ml glass pipette. The vial was capped with a Teflon coated cap and the samples were placed into the Vortex Auto Sampler and left to dissolve for 3 hrs at 140°C while stirring gently. Broad polystyrene samples were also used as controls.

Data Analysis

The polymer samples were successfully analysed by the Triple Detection method. The detector alignment and instrument sensitivity parameters were previously determined using a narrow polystyrene standard. A broad polystyrene standard was used for system verification.

Differential Scanning Calorimetry

About 6.5 mg of the samples were taken for the analysis, with heating & cooling at a rate of 10 °C/min under a nitrogen atmosphere. Each sample was analyzed twice for accuracy, and the average value reported as shown in Table 3.

B. NMR spectra

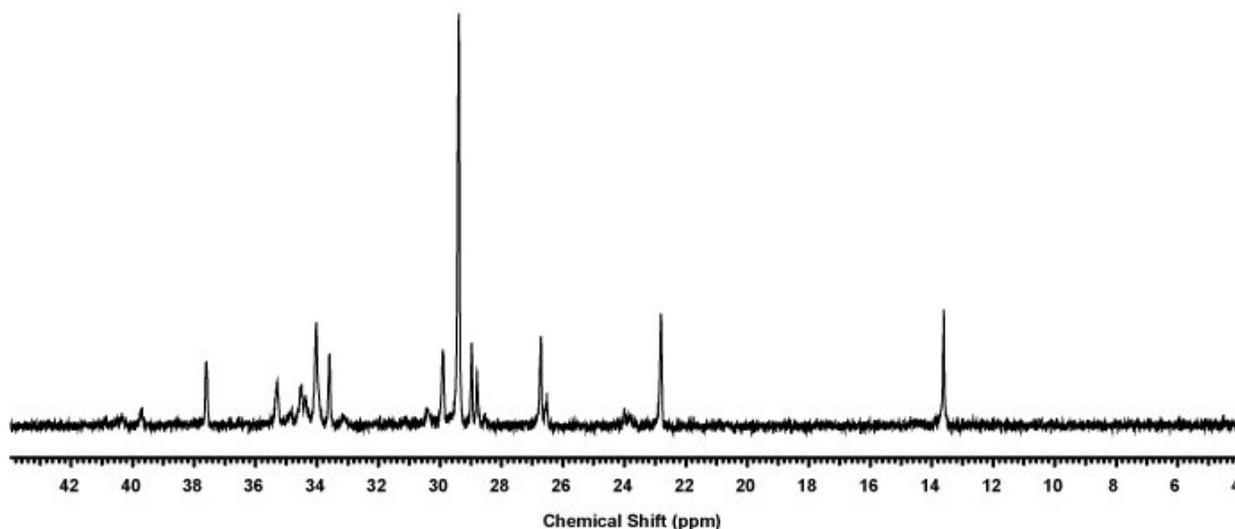


Figure S1: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (130 °C, tetrachloroethane) of LLDPE sample (20% 1-hexene incorporation) prepared using co-supported catalyst system.

C. Kinetic Model

A simplified kinetic model was constructed to help assess the extent to which the co-supported catalysts function independently, as opposed to cooperating and/or interfering with one another. The model consists of three reaction steps: insertion of ethylene into a polymer chain growing at the polymerization catalyst (“pcat”); insertion of 1-hexene into the polymer chain; and trimerization of ethylene to 1-hexene at the trimerization catalyst (“tcat”). The amounts of ethylene and hexene incorporated into polymer chains (“peth” and “phex” respectively), and the amount of free hexene (“hex”), will be determined by the following differential equations, assuming polymer growth and trimerization are independent first- and second-order processes respectively:

$$\frac{d[\text{peth}]}{dt} = k_1 [\text{ethylene}][\text{pcat}]$$

$$\frac{d[\text{phex}]}{dt} = k_2 [1\text{-hexene}][\text{pcat}]$$

$$\frac{d[\text{hex}]}{dt} = k_t [\text{ethylene}]^2 [\text{tcat}] - k_2 [1\text{-hexene}][\text{pcat}]$$

This model incorporates a number of simplifying assumptions, several of which are known to be only approximately valid at best, but which hopefully are good enough to answer the basic questions posed. First, all amounts of substances (including solids) are treated as effective concentrations of soluble species; this neglects any effects of mass transfer to and from the support surface. Second, catalyst “concentrations” are taken to be constant over the life of the run; the trimerization catalyst in particular is known to exhibit both gradual initiation and deactivation during such periods.⁵ Two others are discussed below.

Numerical integration of the differential equations was performed by Euler’s method, using a simple home-made BASIC program, and parameters adjusted to achieve the best fit to experimental results. All reactions modeled used 300 mg catalyst, with a total of 18 μ moles Ti/g, in 0.05 L of toluene, corresponding to a total effective [Ti] of 108 μ M, divided between [pcat] and [tcat] as appropriate to the particular experiment; at 1 atm [ethylene] = 0.142 M.

Test 1: Polymerization catalyst only; ethylene only:

To match the experimental polymer yield of 6.55 g after 3h, $k_1 = 24 M^{-1}s^{-1}$.

Test 2: Polymerization catalyst only; ethylene + 90 mM 1-hexene.

The predicted polymer yield substantially exceeds the experimental value (1.61 g with 5.1 mol% 1-hexene incorporation, suggesting that 1-hexene competes with ethylene for coordination to the polymerization catalyst and thus inhibits ethylene polymerization. There are a number of possible ways to build such behavior into the model, but the simplest (though again, only approximately valid) is to modify the first two equations by multiplying by the terms [ethylene]/([ethylene]+[hexene]) and [hexene]/([ethylene]+[hexene]) respectively. With that adjustment, good agreement with both the total polymer weight and 1-hexene incorporation was achieved with a value of $k_2 = 4 M^{-1}s^{-1}$. Thus, within the limits of these approximations, 1-hexene is incorporated into a chain around 1/6 as rapidly as ethylene.

Test 3: Co-supported s-FI(Ti)(1)-(Cp*SiNR)Ti(3); ethylene only:

The experimental results (polymer yield 3.21 g; 7.6 mol % 1-hexene in polymer; 129 mM 1-hexene in solution) were reproduced very closely (see Table 2 in main text) with $k_t = 50 M^2s^{-1}$ and the above values for k_1 and k_2 . No correction was made for the competing formation of decenes by co-trimerization of 1-hexene with two ethylenes; under these conditions that would not be expected to be a major factor.⁵

Test 4: Co-supported s-FI(Ti)(1)-(Cp*SiNR)Ti(3); ethylene + 50 mM $^{13}CH_2=CHC_4H_9$:

Experimental results for 1 and 2 h runs are compared to model predictions, using the above values for all three rate constants, in Table 1 of the main text; reasonably good agreement was achieved for polymer yield, incorporation of 1-hexene into polymer, [hexene] in solution, and amount of label in both polymer and free hexene.

For the case of cooperative behavior — that is, if some fraction of hexene produced by trimerization gets transferred directly to a growing polymer chain without leaving the support surface — the model was modified by adding a term to each of the last two equations as follows, in which x = probability of 1-hexene being incorporated into polymer without going into solution:

$$\frac{d[\text{phex}]}{dt} = k_2[1\text{-hexene}][\text{pcat}] + k_t[\text{ethylene}]^2[\text{tcat}]x[\text{pcat}]$$

$$\frac{d[\text{hex}]}{dt} = k_t[\text{ethylene}]^2[\text{tcat}](1-x)[\text{pcat}] - k_2[1\text{-hexene}][\text{pcat}]$$

Parameters k_2 and k_t were optimized for this revised model and a value of $x = 0.5$ by fitting predictions to the results of tests 2 and 3 above; the best match was not as good as for the baseline case of $x = 0$, but not so much worse as to allow any confident conclusion. However, when this model was applied to the labeling studies of test 4, there were strong discrepancies between prediction and experiment, particularly with regard to the *relative* labeling of free and polymerized 1-hexene, as discussed in the main text, providing good evidence against any significant cooperative behavior.

D. Polymer Properties

Table S1: LLDPE samples used for analysis

Entry ^a	Sample ID	(FI)Ti:(Cp*SiNR)Ti	Ti loading (μmol/g) ^b	Amount (mg) ^c	Yield (g) ^d	1-hexene incorporation ^e
1	DA_01_67	1:2	18	620	10.1	20%
2	DA_01_71	1:2.6	18	598	6.66	16%
3	DA_01_77	1:3	18	590	11.1	7.0%
4	DA_01_61	1:4	18	597	3.81	1.8%
5	DA_01_47	1:5	18	599	4.97	1.2%
6	DA_01_123	1:3	18	304	8.65	20%

^aReactions in entries 1-5 were carried out as a slurry with 100 mL of toluene under 1 atmosphere ethylene pressure. Entry 6 was carried out at 3.4 atmosphere ethylene pressure with 50 mL of toluene.

^bThe total titanium content in the co-supported catalyst. ^cThe amount of the co-supported silica catalyst used in the experiment. ^dTotal dry weight of isolated polymer. ^e1-Hexene incorporation as determined using quantitative ¹³C{H} NMR spectroscopy.

GPC Analysis

Table S2: Number averaged molecular weights (M_n) and polydispersity (PDI) for LLDPE samples

Sample	M_n ($\times 10^5$ Da)	PDI	T_m (°C)
DA_01_47	4.14	2.38	119
DA_01_61	3.67	3.20	117
DA_01_67	3.69	1.88	114
DA_01_71	2.57	2.77	116
DA_01_77	4.03	2.27	115
DA_01_123	4.11	2.12	115

E. References

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