



Research article

Elongation and branching of α -olefins by ethylene employing an easily accessible Zr catalyst

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ABSTRACT

Selective co-oligomerizations between α -olefins and ethylene are of high interest since they allow to extend the α -olefin scope employing inexpensive and abundantly available ethylene. Here we report on an easily accessible zirconium catalyst that permits the co-oligomerization of 1-hexene and ethylene with an activity of 2200 kg/mol h bar and a co-oligomer selectivity of 65 mol%. In more detail, we report synthesis and structure of six novel Zr precatalysts, their ethylene homo-oligomerization behavior and the co-oligomerization of the most promising of the six precatalysts. Criteria were activity and selectivity (α -value). Some of the Zr catalyst systems introduced here show an extremely high activity in ethylene homo-oligomerization up to 96,600 kg/mol h bar.

1. Introduction

α -Olefins are important bulk and fine chemicals employed for the synthesis of plastics, detergent alcohols and lubricants for instance [2]. The synthesis of α -olefins from ethylene is carried out in megaton scale annually and is a key application of homogenous catalysis [3]. The selective or on-purpose synthesis of α -olefins from ethylene is restricted to three examples: 1-butene, 1-hexene and 1-octene, all having a linear structure [4]. We introduced a broadly applicable α -olefin elongation and branching reaction recently [1]. This reaction permits access to branched α -olefins employing ethylene. The introduction of branches is the key to synthesize synthetic lubricants [5], highly transparent plastics [6] and membranes for gas separation [7]. Selectively branched α -olefins are also of interest for functionalization chemistry, largescale reaction such as hydroformylation [8]. Unfortunately, the titanium catalyst (family) employed in our elongation and branching reaction recently is challenging to be synthesized [1]. The use of a temperature and light sensitive Ti precursor namely $\text{Ti}(\text{Bn})_3\text{Cl}$ (Bn = benzyl) is essential and the two N ligands are introduced by two different types of reaction – toluene elimination and salt metathesis. Herein, we report on an easily accessible zirconium catalyst that permits the co-oligomerization of 1-hexene and ethylene with an activity of 2200 kg/mol h bar and a co-trimer selectivity of 65 mol%. Six novel Zr precatalysts were introduced and their ethylene homo-oligomerization behavior was investigated to identify the most promising co-oligomerization precatalysts. Activity and α -value were used as

criteria. Some of the Zr catalyst systems introduced here show an extremely high activity in ethylene homo-oligomerization.

2. Material and methods

2.1. General procedure

All manipulations were performed with the rigorous exclusion of oxygen and moisture by using standard Schlenk type glassware on a dual-manifold Schlenk line and glovebox techniques (mBraun 120-G) with a high-capacity circulation (<0.1 ppm O_2) under an atmosphere of argon or nitrogen.

2.2. Materials

Deuterated solvents were obtained from Eurisotop, degassed, distilled and stored over activated 3 Å molecular sieves prior to use. Solvents were dried and purified by distillation from LiAlH_4 , potassium, Na/K alloy or sodium benzophenone ketyl under argon atmosphere and stored over activated 3 Å molecular sieves before use. 1-Pentene and 1-hexene were obtained from ACROS and dried and purified by distillation from LiAlH_4 under argon atmosphere and stored over activated 3 Å molecular sieves before use. Ethylene (3.5, Linde AG) was passed over columns of BASF R3-11 supported Cu oxygen scavenger and Al_2O_3 (-Fluka). All other reagents and starting materials were purchased from commercial vendors with a purity of at least 97 % and used without

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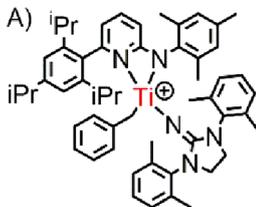
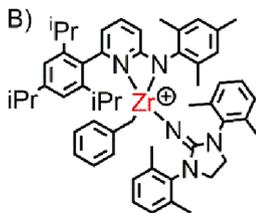
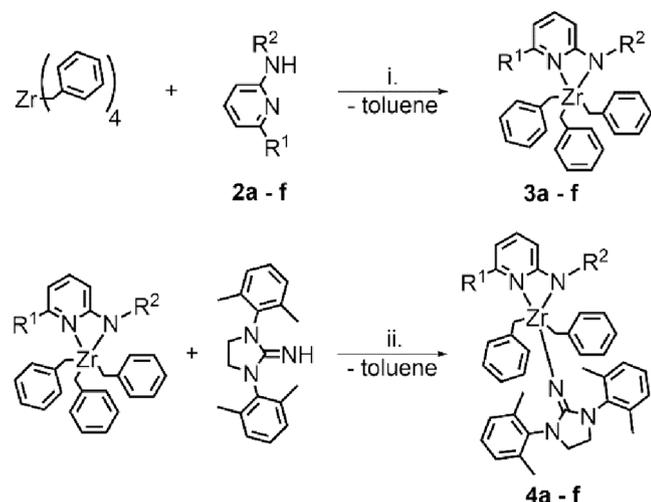
A) 	Selectivity [mol.-%]		
			tetramers
Cat. 1; Dietel et al.	16	72	7
B) 	12	64	17

Fig. 1. Elongation and branching of 1-hexene by two ethylene molecules. A) State of the art [1] and B) work reported here. Selectivity of co-dimer, co-trimer and co-tetramers are given and R = butyl.



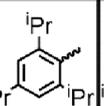
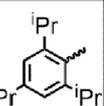
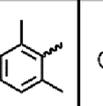
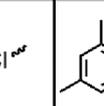
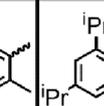
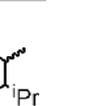
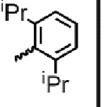
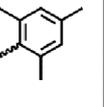
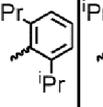
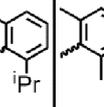
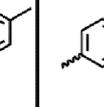
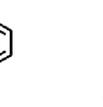
Precat.:	a	b	c	d	e	f
R ¹						
R ²						

Fig. 2. Synthesis of the precatalysts 4a-f; i. = *n*-hexane, 60 °C, 24 h; ii. = toluene, 60 °C, 24 h.

further purification unless otherwise noted.

2.3. Synthetic procedure

2.3.1. Precatalyst synthesis

Here the synthesis of precatalyst 4b is described, the synthesis of the precatalysts 4a,c-f was performed analogously and is given in the Supporting Information. All precursors were synthesized according to the literature [9,10,11,12,13].

Toluene (5 mL) was added to a mixture of 3b (93.0 mg; 0.12 mmol;

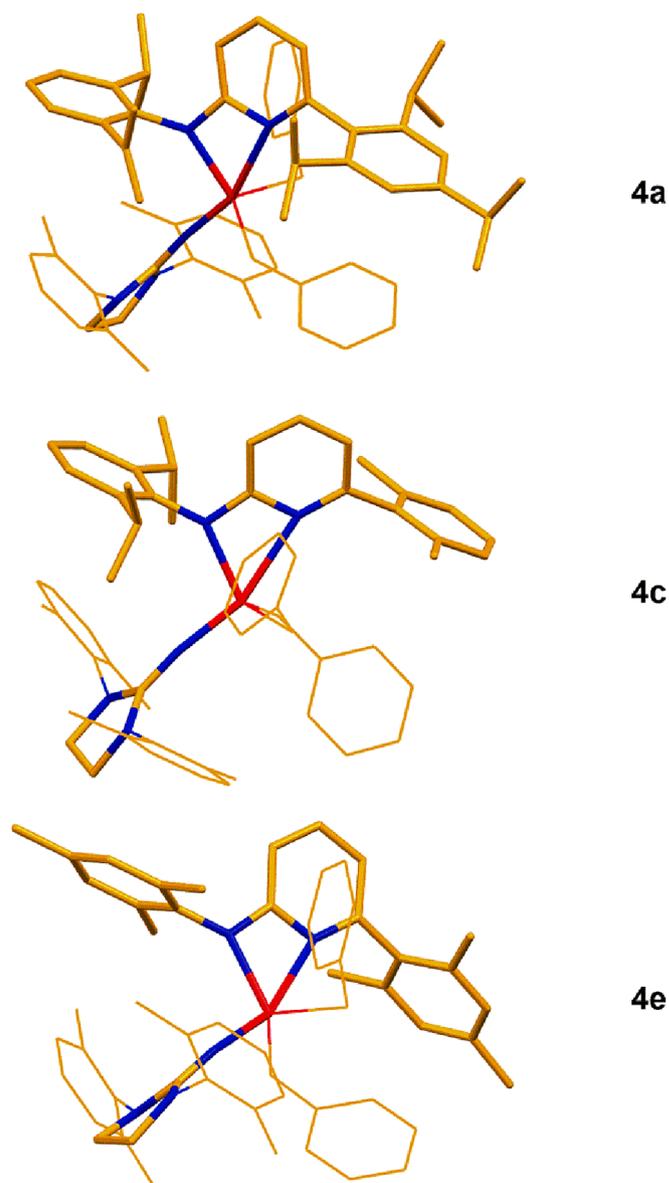
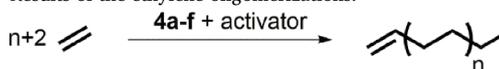


Fig. 3. Molecular structures of the complexes 4a, 4c and 4e. Color code: Zr = red, N = blue, C = orange. Hydrogen atoms are omitted for clarity.

Table 1

Results of the ethylene oligomerizations.



Entry	Precat.	T [°C]	V _{et} [L _N]	Activity [kg _{et} mol ⁻¹ h ⁻¹ bar ⁻¹]	α-value
1	4a	50	7.7	96,600	0.56
2	4b	50	2.5	31,300	0.33
3	4c	50	6.9	86,350	0.57
4	4d	50	0.9	12,300	0.83 ^[a]
5	4e	50	0.4	5600	0.46
6	4f	50	0.2	3100	0.94 ^[b]
7 ^[c]	4b	25	2.6	9900	0.27
8 ^[c]	4b	0	2.7	10,400	0.18
9 ^[c]	4b	-15	2.2	8300	0.10

n_{precatalyst} = 0.2 μmol; n_{ammoniumborate} = 0.22 μmol; t = 15 min; p_{et} = 1 bar; n_{TIBA} = 100 μmol; V_{toluene} = 150 mL; V_{et}: ethylene volume consumed during catalysis; [a]: 1.10 g polymer; [b]: 0.05 g polymer; [c]: n_{precatalyst} = 1.0 μmol; n_{aniliniumborate} = 1.1 μmol; t = 10 min; n_{TIBA} = 25 μmol; V_{toluene} = 50 mL.

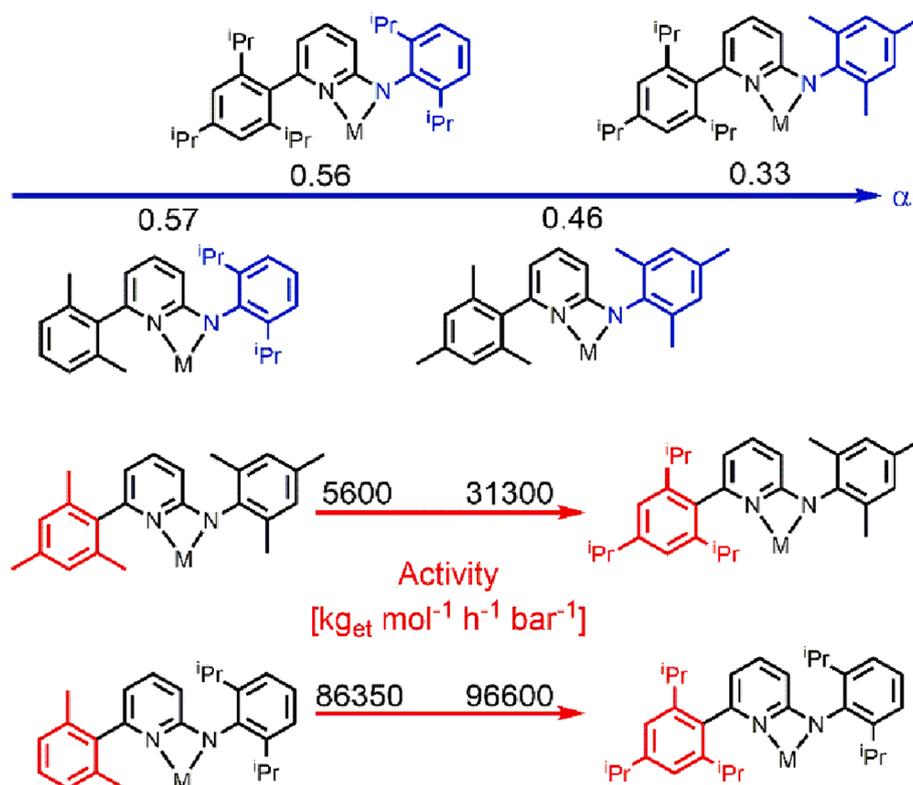


Fig. 4. Qualitative description of the influence of the substituents at the Ap ligand (M = ImiZrBn₂).

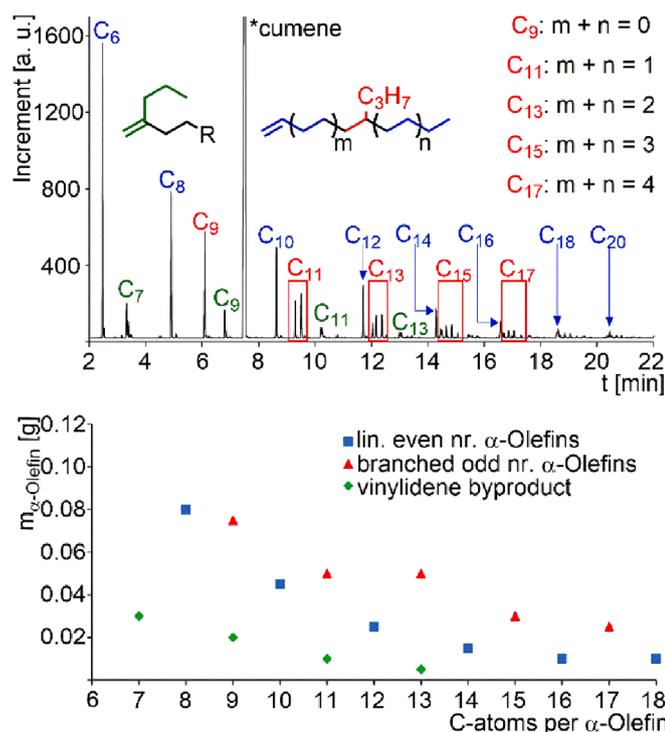


Fig. 5. GC of the products synthesized by co-oligomerization of ethylene and 1-pentene using **4c**, $V_{\text{et}} = 0.5 L_{\text{n}}$, $p_{\text{et}} = 1$ bar. Mass of the branched and linear α -olefins and the vinylidene terminated byproducts plotted versus the C-atoms per α -olefin species, (lin. = linear, nr. = numbered).

1.0 eq.) and 1,3-bis(2,6-dimethylphenyl)imidazolidin-2-imine (31.0 mg; 0.12 mmol; 1.0 eq.) at room temperature. The resulting solution was stirred for 24 h at 60 °C. The mixture was evaporated to dryness and the resulting residue was washed with hexane (1 mL) affording **4b** as a yellow solid. Yield 94.0 mg (0.10 mmol; 83 %).

2.3.2. Olefin oligomerization

Stock solutions of the precatalysts **4a-f** (0.001 M), the cocatalyst/activator [(*N,N*-dimethylanilinium)tetrakis(pentafluorophenyl)borate (aniliniumborate) or *N,N,N*-dialkylmethylammonium(tetrakis(pentafluorophenyl)borate R = C₁₆H₃₃ – C₁₈H₃₇ (ammonium-borate)] (0.001 M) and the scavenger triisobutylaluminum (TIBA) (0.025 M) were prepared in toluene. For all ethylene oligomerizations, an evacuated 300 mL and for all co-oligomerizations an evacuated 50 mL glass autoclave (BüchiGlasUster) was used. The reactions were stirred using a mechanical stirrer (1000 rpm) and were tempered by an external water bath. The ethylene gas flow was monitored by a Bronkhorst High-Tech El-Flow unit.

For ethylene homo-oligomerizations, the autoclave was filled with 150 mL of toluene and saturated with ethylene at 1 bar.

For ethylene 1-hexene co-oligomerizations, the autoclave was pressurized with ethylene at 1 bar and a mixture of 50 mmol (6.5 mL) of 1-hexene and 4.5 mL toluene was injected. For ethylene 1-pentene co-oligomerization stock solutions were prepared using 1-pentene as solvent. The evacuated autoclave was pressurized with ethylene at 1 bar and 17 mL of 1-pentene were injected.

For all oligomerizations, the scavenger-, cocatalyst- and catalyst stock solutions were injected subsequently. Then the respective ethylene pressure was adjusted and the ethylene consumption was recorded.

The oligomerizations were terminated by stopping the ethylene flow and injecting demineralized H₂O (1 mL) and the cumene standard (1.0 g) into the autoclave. The product solutions were solvent extracted with demineralized H₂O and the organic phase was separated.

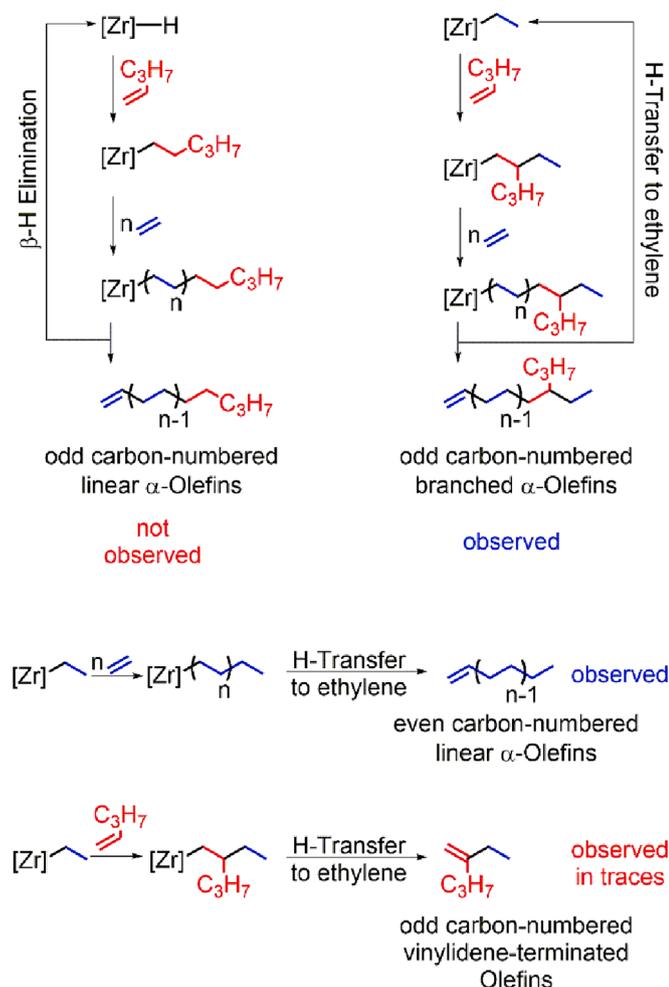


Fig. 6. Identification of the chain termination reaction by product analysis.

3. Results and discussion

3.1. Precatalysts synthesis

Precatalysts **4a-f** are accessible in a two steps synthesis, as depicted in Fig. 2. The zirconium precursor $[\text{ZrBn}_4]$ ($\text{Bn} = \text{benzyl}$) [9], the aminopyridines **2a-f** [10] and 1,3-bis(2,6-dimethylphenyl)imidazolidin-2-imine (Imi-H) [11] were used for complex syntheses. The complexes **3a-f** were synthesized via toluene elimination in *n*-hexane as the solvent [12]. Treatment of one equivalent of Imi-H with **3a-f** in toluene resulted in complexes **4a-f**. The complexes **4a-f** were characterized by elemental analysis, ^1H - and ^{13}C NMR spectroscopy; (for ^1H - and ^{13}C NMR spectra see Supporting Information). Crystals suitable for x-ray single crystal

structure analysis were grown by layering a saturated toluene solution with *n*-hexane. Molecular structures of complexes **4a**, **4c** and **4e** are depicted in Fig. 3. The molecular structure of **4a**, **4c** and **4e** display a distorted trigonal-bipyramidal geometry. The pyridine nitrogen atom and the Imi ligand align at the axial positions with an equatorial plane formed by the two CH_2 -groups of the benzyl moieties and the Ap ligand's amide nitrogen atom.

3.2. Ethylene oligomerizations

Firstly, we were interested in the performance of precatalysts **4a-f** in the homo-oligomerization or polymerization of ethylene after activation with ammonium borates, especially in their activity. All catalysts oligomerize ethylene to yield linear α -olefins. The oligomers produced follow a Schulz-Flory distribution [14] suggesting a Cossee and Arlman type of mechanism analogously to **1** [1,14] and α -value. We calculated the α -value, which is defined as $n(C_{m+2})/n(C_m)$ (n being the amount of substance), by averaging the n ratios from 1-hexene to 1-hexadecene if detectable [15]. The results are listed in Table 1. Precatalysts **4a-c** gave highly active ethylene oligomerization catalysts producing more than 30 t of oligomer per mol catalyst hour and bar. The activities of the other catalysts are significantly lower. The smallest α -value is observed for the catalyst system based on **4b**. Note, that a small α -value is crucial for observing a rather selective co-oligomerizations between α -olefins and ethylene. Temperature dependence studies of the α -value of the catalyst system based on **4b** revealed an increase of the α -value with increasing temperature permitting the reduction of the α -value to 0.1 (90 % 1-butene selectivity) at -15°C . There seems to be an influence of the structure of the Ap-ligand on the product distribution (α -value) and on the catalyst's activity (Fig. 4). The substituent at the amido-N atom of the Ap ligand is colored blue and the substituent at the pyridine unit of the Ap ligand is colored red. A high steric demand of the red fragment seems to result in a higher catalyst activity. Less steric demand of the blue-colored fragment leads to a smaller α -value.

3.3. Ethylene 1-hexene co-oligomerizations

The catalyst system based on precatalyst **4b** was selected for the co-oligomerization of ethylene and 1-hexene based on the low α -value observed in comparison to the other precatalysts (**4a** and **4c-f**). Temperature and ethylene pressure were varied to find options for influencing the selectivity of co-trimer formation. The catalyst activity is above 1000 kg/mol h bar for all runs and can be classified as highly active [16]. A slightly higher activity was observed at 4 bar ethylene pressure in comparison to the 2 bar runs and a significant increase of activity for the runs at 25°C (compared to 0°C). Interestingly, the co-trimer selectivity is similar at 0°C and at 25°C despite the significant change of the α -value (Table 1) and the associated higher by-product formation of longer chain co-oligomers and linear α -olefins. It is compensated by a relatively low co-dimer formation at 25°C in comparison to 0°C . Note that the temperature dependence of the co-dimer

Table 2

Selectivity of the catalyst system based on **4b** for the co-oligomerization of ethylene and 1-hexene. Selectivity of co-dimer, co-trimer and higher α -olefins are shown.

Two runs were averaged. $n \equiv + \text{CH}_2=\text{CH}(\text{CH}_2)_4\text{CH}_3 \xrightarrow{\text{4b} + \text{activator}} \text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{higher branched olefins}$

Entry	T [$^\circ\text{C}$]	P _{et} [bar]	Selectivity [mol.-%]			Activity [$\text{kg}_{\text{et}} \text{mol}^{-1} \text{h}^{-1} \text{bar}^{-1}$]
					higher branched olefins	
1	0	2	18.7 (± 1.2)	65.8 (± 0.9)	15.5 (± 0.4)	1150 (± 10)
2	0	4	16.7 (± 2.0)	66.0 (± 0.9)	17.3 (± 0.6)	2000 (± 500)
3	25	2	11.8 (± 0.3)	64.6 (± 0.1)	23.6 (± 0.2)	2200 (± 60)
4	25	4	10.5 (± 0.7)	63.1 (± 0.5)	26.4 (± 0.2)	2800 (± 120)

$n_{\text{precat } \mathbf{4b}} = 1.0 \mu\text{mol}$; $n_{\text{aniliniumborate}} = 1.1 \mu\text{mol}$; $n_{\text{TIBA}} = 1.1 \mu\text{mol}$; $n_{1\text{-hexene}} = 50 \text{ mmol}$; $V_{1\text{-hexene}} = 6.5 \text{ mL}$; $V_{\text{toluene}} = 8.5 \text{ mL}$; $t = 15 \text{ min}$.

formation of **1** is negligible changing from 18 % at 15 °C to only 15 % at 60 °C [1].

3.4. Mechanical studies

Next, 1-pentene was used as co-monomer. It permits to distinguish between linear (e.g. 1-heptene, 1-nonene, ...) and branched (e.g. 4-ethyl-1-heptene, 4-ethyl-1-nonene, ...) olefins from ethylene/1-pentene co-oligomerization and linear (e.g. 1-hexene, 1-octene, ...) oligomers created by ethylene oligomerization side reaction. Additionally, branched even carbon numbered co-oligomer products (reinsertion of ethylene side reaction based 1-olefins) can be identified. A GC of ethylene 1-pentene co-oligomerization products is depicted in Fig. 5. The odd carbon numbered branched co-oligomers are marked red and the linear products are marked blue. Odd carbon numbered vinylidene terminated byproducts are marked green. Even carbon numbered branched olefins are only detectable in traces, while linear odd carbon numbered products are not observed. For every branched odd carbon numbered co-oligomer containing more than nine carbons, an additional branched species appears, because an ethylene molecule can be possibly inserted before or after the 1-pentene molecule. Referring to the co-oligomer scheme depicted in Fig. 5, a thirteen-carbon containing co-oligomer (C₁₃) for example can consist of m = 2 with n = 0; m = 0 with n = 2 or m = 1 with n = 1. All three C₁₃ species are confirmed by GC. At high 1-pentene concentration, there is a larger mass of branched co-oligomerization products for fractions containing nine or more carbons than linear even carbon numbered byproducts.

The ethylene 1-pentene co-oligomers enable the determination of the chain termination reaction by product analysis. The sequences of olefin insertion during oligomerization and the chain termination reactions relevant to the formation of α -olefins are depicted in the schemes given in Fig. 6. β -H elimination/transfer to ethylene is the only occurring chain termination reaction. Only branched odd carbon numbered ethylene 1-pentene co-oligomers were detected by GC. Linear odd carbon numbered α -olefins need to be detected if β -H elimination (and insertion of 1-pentene) would occur. Vinylidene terminated byproducts are generated if chain termination reaction takes place directly after *head to tail* insertion of an α -olefin. These byproducts are observed in low concentration indicating that chain termination predominantly takes place after the insertion of an ethylene molecule.

4. Conclusion

In summary, we describe homo-oligomerization of ethylene and the co-oligomerization of 1-hexene and ethylene by novel Zr catalysts. The synthesis of the precatalyst is significantly easier than of the related Ti catalysts. Some of the Zr catalysts are highly efficient ethylene oligomerization catalysts. The co-trimer selectivity observed for the most selective catalyst are slightly lower than for **1** (Fig. 1 and Table 2). The co-dimer formation is strongly temperature dependent permitting to work at higher temperature with similar selectivity despite the increase of the α -value. It seems that for catalyst selection the temperature dependence of the α -value and the temperature dependence of the co-trimer/co-dimer selectivity are the key and not just the α -value (at a certain temperature).

CRediT authorship contribution statement

Christian Heber: Data curation, Formal analysis, Investigation, Methodology, Validation, Writing – original draft, Writing – review & editing. **Thomas Dietel:** Investigation, Methodology. **Isabelle Haas:** Investigation, Methodology. **Winfried P. Kretschmer:** Supervision, Writing – review & editing, Conceptualization. **Rhett Kempe:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Validation, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Rhett Kempe reports financial support was provided by Deutsche Forschungsgemeinschaft. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcat.2024.115503>.

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