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Selective ethylene trimerization with a cyclopentadienyl-arene titanatrane catalyst

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Abstract Cyclopentadienyl-arene titanatrane catalysts activated by methylaluminoxane (MAO) cocatalysts were studied for the trimerization of ethylene. The introduction of electron-rich multidentate ligands to the catalysts' active sites resulted in good productivity and selectivity for ethylene trimerization. Various amounts of MAO were tested, and methods of its introduction to the system were varied. It has been shown that pre-alkylation of the catalyst with MAO increases the productivity of ethylene trimerization. The effects of reaction temperature and pressure on 1-hexene productivity and selectivity were also studied. The rate of ethylene conversion was approximately first order with respect to ethylene concentration. 1-Hexene was produced under moderate conditions, allowing energy savings to be gained through lower temperature reactions.

Introduction

The oligomerization of ethylene is one of the most important issues for the synthesis of linear alpha olefins (LAO) in both academia and industry [1, 2]. The selective oligomerization of ethylene has recently attracted considerable attention, as unwanted olefin products would not be produced by selective oligomerization [3]. In particular, 1-hexene can be produced by selective trimerization of ethylene. It is mainly used as a comonomer for the production of linear low-density polyethylene (LLDPE), and its price has been very high owing to the imbalance of supply and demand [4].

The selective trimerization of ethylene can mainly be achieved with chromium Ziegler-type catalysts, consisting of a combination of Cr(III) salts (usually carboxylates) with aluminum alkyls in conjunction with a Lewis basic donor (usually pyrroles or 1,2-diethoxyethane). The only current industrial process that can produce 1-hexene by ethylene trimerization is based on this chromium catalyst [1, 2, 5–8].

Cyclopentadienyl-arene titanium complexes [η^5-C_5H_4–(bridge)–Ar]–$TiCl_3$, activated by methylaluminoxane (MAO), have been reported by Hessen et al. to form highly active catalysts for the trimerization of ethylene [4, 9–11]. This discovery has attracted many researchers' interest in developing ethylene trimerization catalysts.

Efforts to develop catalysts for ethylene trimerization have largely focused on the modification of the cyclopentadienyl ring by the addition of a pendant group that can coordinate to the metal center; or the introduction of a bridge between the metal and the cyclopentadienyl ring [3, 12].

However, there appear to be no other studies of trimerization catalysts involving direct electronic modification of the catalytically active site by the introduction of electron-rich multidentate ligands in place of the monodentate Cl_3 ligands. In this regard, the potentially tetradentate trianionic triethoxyamine ($N(CH_2CH_2O)_3^{3-}$, TEA), which is the fully deprotonated form of triethanolamine, is potentially suitable for modifying the active site of ethylene trimerization catalysts.

This work reports the synthesis of cyclopentadienyl-arene titanatrane catalysts for selective ethylene trimerization. Titanatrane denotes cyclic titanium ethers of tris(2-

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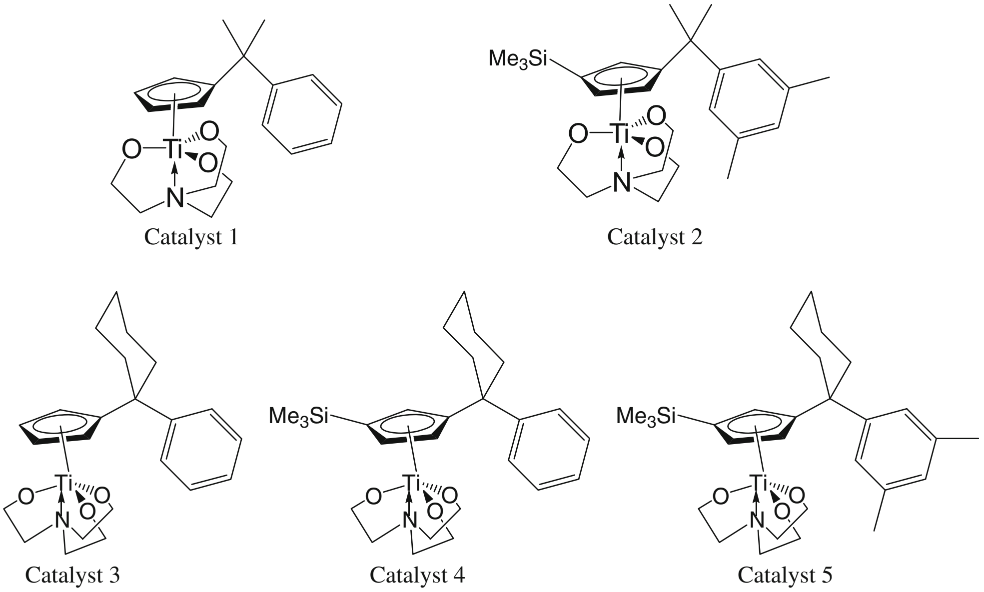

Catalyst 1 Catalyst 2

Catalyst 3 Catalyst 4 Catalyst 5

Scheme 1 Ethylene trimerization catalysts

oxyalkyl)amine [13]. Cyclopentadienyl-arene titanatrane complexes were synthesized and tested for ethylene trimerization (Scheme 1).

Experimental

General procedures

All manipulations of water- and/or air-sensitive compounds were performed using standard Schlenk and glove-box techniques under deoxygenated argon or nitrogen [14]. The solvents for synthesis, tetrahydrofuran (THF), *n*-hexane, *n*-pentane, diethyl ether, and methylene chloride (CH_2Cl_2), were distilled through an activated alumina column and dried over molecular sieves (5 Å, Yakuri Pure ChemicalsCo) to eliminate moisture [15]. Chloroform-d($CDCl_3$) and benzene-d6(C6D6) for NMR analysis were acquired from Cambridge Isotope Laboratories and dried over molecular sieves (5 Å, Yakuri Pure ChemicalsCo) [15]. *n*-Butyllithium (2.5 M in *n*-hexane), phenyllithium (1.8 M solution in dibutyl ether), 1-bromo-3,5-dimethylbenzene, 6,6-dimethylfulvene, triethanolamine, triethylamine, 6,6-pentamethylfulvene, trimethylsilyl chloride, $TiCl_4$, and magnesium sulfate were acquired from Sigma-Aldrich and used as received. The MAO cocatalyst (10 wt.% aluminum in toluene) was purchased from Albemarle. Ethylene was distilled through an alumina column and Cu-supported oxygen scavenger before use [15].

NMR spectra were recorded on a Bruker Avance 400 Spectrometer at 25 °C. Chemical shifts (δ) are reported for $CDCl_3$ (7.24 ppm) and C_6D_6 (7.16 ppm).

Synthesis

(η^5-$C_5H_4CMe_2Ph$)$TiCl_3$, [η^5-(3-$SiMe_3$)$C_5H_3CMe_2$–3,5-Me_2-C_6H_3]$TiCl_3$, {η^5-$C_5H_4C[(CH_2)_5]Ph$}$TiCl_3$, [η^5-(3-$SiMe_3$)$C_5H_3C[(CH_2)_5]Ph$}$TiCl_3$, and {η^5-(3-$SiMe_3$)$C_5H_3C[(CH_2)_5]$–3,5-$Me_2C_6H_3$}$TiCl_3$ were synthesized by a procedure reported elsewhere in the literature [4, 9–11].

Synthesis of (η^5-$C_5H_4CMe_2Ph$)Ti(TEA)

In 50 ml of toluene, 6 mmol (2.016 g) of (η^5-$C_5H_4CMe_2Ph$)$TiCl_3$ was dissolved and cooled to −78 °C. Then, 6 mmol of triethanolamine and 18 mmol of triethylamine were added dropwise to the solution. The mixture was allowed to warm up to room temperature and stirred for 12 h. The orange suspension was filtered through a Celite bed, and the volatiles were removed under vacuum. The desired orange product in 60 % yield (3.6 mmol, 1.357 g) resulted after stripping with *n*-hexane.

^{1}H NMR(400 MHz, $CDCl_3$): $\delta = 6.70$–6.48(*m*, 5H, ArH), 4.28(*m*, 6H, NCH_2CH_2O), 3.08(*m*, 6H, NCH_2CH_2O), 1.70 (*s*, 6H, $C(CH_3)_2$); $^{13}C\{^1H\}$ NMR(100 MHz, $CDCl_3$): $\delta =$ 154.66 (Ph_{ipso}), 147.63 (Cp_{ipso}), 128.54 (*o*-Ph), 126.67(*p*-Ph), 125.89 (*m*-Ph), 123.55 (Cp), 121.81 (Cp), 70.52(NCH_2CH_2O), 55.45(NCH_2CH_2O), 41.00 (CMe_2Ph), 28.80 (Me); Element Analysis: Calcd for $C_{20}H_{27}NO_3Ti$: C 63.67, H 7.21, N 3.71. Found: C 63.57, H 7.13, N 3.67.

Synthesis of [η^5-(3-$SiMe_3$)$C_5H_3CMe_2$–3,5-$Me_2C_6H_3$]Ti(TEA)

In 50 ml of toluene, 6 mmol (2.616 g) of [η5-(3-$SiMe_3$)$C_5H_3CMe_2$–3,5-$Me_2C_6H_3$]$TiCl_3$ was dissolved and cooled to −78 °C. Then, 6 mmol of triethanolamine and 18 mmol of triethylamine were added dropwise to the solution. The mixture was allowed to warm up to room temperature and stirred for 12 h. The orange suspension was filtered through a Celite bed and the volatiles were removed under vacuum. The desired ivory-colored product in 35 % yield (2.1 mmol, 1.002 g) resulted after stripping with *n*-hexane.

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.87$(*s*, 2H, Ar–*o*), 6.77(*s*, 1H, Ar–*p*), 6.35–6.37(*q*, 3H, Cp), 4.26–4.3 (*q*, 6H, NCH_2CH_2O), 2.26–2.96(*t*, 6H, NCH_2CH_2O), 2.27 (*s*, 6H, $ArCH_3$), 1.7 (*s*, 6H, $C(CH_3)_2$) 0.18(*s*, 9H, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR(100 MHz, $CDCl_3$): $\delta = 152.14$, 138.82, 136.95(Ar and Cp C_{ipso}), 128.14, 127.01, 124.48, 122.63, 120.25(Ar CH and Cp CH), 70.73(NCH_2CH_2O), 55.73(NCH_2CH_2O), 40.12($C(CH_3)_2$), 29.78, 29.54($C(CH_3)_2$), 21.71($ArCH_3$), −0.149($Si(CH_3)_3$); Element Analysis: Calcd for $C_{25}H_{39}NO_3SiTi$: C 62.88, H 8.23, N 2.93. Found: C 62.76, H 8.25, N 2.96.

Synthesis of $\{\eta 5\text{-}C_5H_4C[(CH_2)_5]Ph\}Ti(TEA)$

In 50 ml of toluene, 1.92 mmol (0.722 g) of $\{\eta^5\text{-}C_5H_4C[(CH_2)_5]Ph\}TiCl_3$ was dissolved and cooled to −78 °C. Then, 6 mmol of triethanolamine and 18 mmol of triethylamine were added dropwise to the solution. The mixture was allowed to warm up to room temperature and stirred for 12 h. The orange suspension was filtered through a Celite bed and the volatiles were removed under vacuum. The desired orange product in 60 % yield (1.152 mmol, 0.481 g) resulted after stripping with *n*-hexane.

^{1}H NMR(400 MHz, $CDCl_3$): δ 7.45(*d*, 2H, ArH), 7.26(*d*, 2H, ArH), 7.15(*m*, 1H, ArH), 6.18(*s*, 2H, Cp), 6.09(*s*, 2H, Cp), 4.17(*m*, 6H, NCH_2CH_2O), 2.85(*m*, 6H, NCH_2CH_2O), 2.65(*d*, 2H, -$(CH_2)_5$), 2.02(t, 2H, –$(CH_2)_5$), 1.56(*b*, 3H, –$(CH_2)_5$), 1.39(*m*, 3H, –$(CH_2)_5$);); $^{13}C\{^1H\}$ NMR(100 MHz, $CDCl_3$): $\delta = 156.0$, 142.1 (Ph and Cp C_{ipso}), 129.2 (Ph *o*–CH), 127.9 (Ph *m*–CH), 126.8 (Ph *p*–CH), 123.2, 120.9 (Cp CH), 70.55(NCH_2CH_2O), 55.35 (NCH_2CH_2O), 45.1 ($C[(CH_2)_5]$), 35.8 (α–CH_2), 26.1 (γ-CH_2), 22.4 (β–CH_2); Element Analysis: Calcd for $C_{23}H_{31}NO_3Ti$: C 66.19, H 7.49, N 3.76. Found: C 66.11, H 7.41, N 3.68.

Synthesis of $[\eta^5\text{-}(3\text{-}SiMe_3)C_5H_3C[(CH_2)_5]Ph\}Ti(TEA)$

In 50 ml of toluene, 1.94 mmol (0.869 g) of $[\eta^5\text{-}(3\text{-}SiMe_3)C_5H_3C[(CH_2)_5]Ph\}TiCl_3$ was dissolved and cooled to −78 °C. Then, 6 mmol of triethanolamine and 18 mmol of triethylamine were added dropwise to the solution. The mixture was allowed to warm up to room temperature and stirred for 12 h. The orange suspension was filtered through a Celite bed and the volatiles were removed under vacuum. The desired ivory-colored product in 60 % yield (1.164 mmol, 0.569 g) resulted after stripping with *n*-hexane.

^{1}H NMR(400 MHz, $CDCl_3$): δ 7.44(*d*, 2H, ArH), 7.24(*d*, 2H, ArH), 7.08(*t*, 1H, ArH), 6.29(*s*, 1H, Cp), 6.17(*s*, 2H, Cp), 4.14(*m*, 6H, NCH_2CH_2O), 2.82(*m*, 6H, NCH_2CH_2O), 2.71(*d*, 1H, −$(CH_2)_5$), 2.57(*d*, 1H, –$(CH_2)_5$), 2.06(*m*, 2H, –$(CH_2)_5$), 1.53(br, 3H, –$(CH_2)_5$), 1.4(*m*, 3H, –$(CH_2)_5$);); $^{13}C\{^1H\}$ NMR(100 MHz, $CDCl_3$): $\delta = 146.04$, 139.58(Cp and Cp_{ipso}), 128.37, 128.31, 125.01(Ar), 121.64, 120.38, 119.8(Cp), 70.58(NCH_2CH_2O), 55.52(NCH_2CH_2O), 46.07($C[(CH_2)_5]$), 37.05, 36.87(α–CH_2), 26.9(γ–CH_2), 23.08(β–CH_2), −0.087 ($Si(CH_3)_3$); Element Analysis: Calcd for $C_{26}H_{39}NO_3SiTi$: C 63.79, H 8.03, N 2.86. Found: C 63.71, H 7.95, N 2.81.

Synthesis of $\{\eta^5\text{-}(3\text{-}SiMe_3)C_5H_3C[(CH_2)_5]\text{–}3,5\text{-}Me_2C_6H_3\}Ti(TEA)$

In 50 ml of toluene, 1.22 mmol (0.581 g) of $\{\eta^5\text{-}(3\text{-}SiMe_3)C_5H_3C[(CH_2)_5]\text{–}3,5\text{-}Me_2C_6H_3\}TiCl_3$ was dissolved and cooled to −78 °C. Then, 6 mmol of triethanolamine and 18 mmol of triethylamine were added dropwise to the solution. The mixture was allowed to warm up to room temperature and stirred for 12 h. The orange suspension was filtered through a Celite bed and the volatiles were removed under vacuum. The desired ivory-colored product in 60 % yield (0.732 mmol, 0.379 g) resulted after stripping with *n*-hexane.

^{1}H NMR(400 MHz, $CDCl_3$): δ 7.42(*s*, 2H, ArH), 6.92(*s*, 1H, ArH), 6.5(*s*, 1H, Cp), 6.39(*s*, 1H, Cp), 6.35(*s*, 1H, Cp), 4.38(*m*, 6H, NCH_2CH_2O), 3.24(*m*, 6H, NCH_2CH_2O), 2.85(*d*, 1H, –$(CH_2)_5$), 2.77(*d*, 1H, –$(CH_2)_5$), 2.46(*s*, 6H, 2Me), 2.42(*t*, 1H, –$(CH_2)_5$), 2.16(*t*, 1H, –$(CH_2)_5$), 1.72(br, 3H, –$(CH_2)_5$), 1.48(br, 3H, –$(CH_2)_5$), 0.25(*s*, 9H, $SiMe_3$); $^{13}C\{^1H\}$ NMR(100 MHz, $CDCl_3$): $\delta = 146.24$, 139.6(Cp and Cp_{ipso}), 128.38, 128.32, 125.03(Ar), 121.66, 120.39, 119.8(Cp), 70.6(NCH_2CH_2O), 55.57(NCH_2CH_2O), 46.09 ($C[(CH_2)_5]$), 37.08, 36.89(α–CH_2), 27.3(γ–CH_2), 23.08 (β–CH_2),), 21.65($ArCH_3$), −0.085($Si(CH_3)_3$); Element Analysis: Calcd for $C_{28}H_{43}NO_3SiTi$: C 64.97, H 8.37, N 2.71. Found: C 64.92, H 8.25, N 2.78.

Ethylene trimerization with MAO as cocatalyst

The trimerization of ethylene was carried out in a 2L autoclave equipped with an agitator after pre-heating at 120 °C and cooling to the required temperature. A volume of 500 ml of toluene and MAO was injected into the reactor under nitrogen atmosphere and pressurized with ethylene to the required pressure. After equilibrating for 20 min, the catalyst solution with toluene (including MAO in some cases) was injected into the reactor. The reaction pressure was kept constant with an ethylene feed during the trimerization reaction. After the run time, the reactor was depressurized and ethanol was injected to deactivate the catalyst and the MAO. The reaction products consisted of three fractions: 1-hexene (trimers of ethylene), 1-decene (cotrimers of ethylene and 1-hexene), and polyethylene (1–2 wt. %). The liquid fraction of the product was collected and filtered for GC analysis using cyclooctane as internal standard. Integration of cyclooctane, 1-hexene, and 1-decene peaks in the GC gives the amount of 1-hexene and 1-decene. After the polymer was separated from the liquid mixture, it was stirred in acidic ethanol for 10 min, repeatedly rinsed with ethanol, and dried under vacuum.

Results and discussion

Effects of triethoxyamine ligands

The effects of replacing the Cl_3 ligands with triethoxyamine ligands in the trimerization catalyst were tested by studying catalysts 1–5 with cyclopentadienyl-arene titanium chloride catalysts 6–10. In this paper, productivity is defined as the amount of 1-hexene with 1 mmol of catalyst an hour, and selectivity is the 1-hexene portion of all the reaction products. From the results in Table 1, the introduction of the triethoxyamine ligands to the active sites had a beneficial influence on the productivity of the 1-hexene, but had little influence on the selectivity. The potentially tetradentate electron-rich trianionic triethoxyamine may be important in selective ethylene trimerization.

Of the catalysts with triethoxyamine ligands, catalysts 1 and 2 showed the best productivity and selectivity. They both contained CMe_2-bridges between the cyclopentadienyl and arene moieties; catalysts 3, 4, and 5 had $C(CH_2)_5$-bridges. The CMe_2-bridge likely provided stronger arene coordination in the cationic active sites than $C(CH_2)_5$-bridges.

The effects of substituents on the catalysts' cyclopentadienyl moieties were probed by comparison of catalysts 1 and 2 and catalysts 3 and 4. The $SiMe_3$-substituted catalysts showed slightly improved activity and selectivity over the non-substituted catalysts.

Each catalyst produced 1–2 wt.% polyethylene byproducts with molecular weights in the range of 400,000–600,000 g/mol. Polyethylene from catalysts 1 and 2 had lower Tm (127–128 °C) than that from catalysts 3, 4, and 5 (130–131 °C). Catalysts 1 and 2 produced more 1-hexene that was used as a co-monomer, which lowered the Tm.

Effects of MAO

Some attention has been paid to the role of MAO in the catalysts with Ti–O bonds [16–18]. When the catalyst is activated using MAO, the cocatalyst can induce Ti–O bonds to open up a site for insertion. It is reported that the cleavage of the third arm of the ligand by MAO can make way for monomer incorporation. So MAO was used as a cocatalyst in the present catalysis system. In the absence of MAO, there was no activity with these catalysts.

As shown in Table 2, it is clear that the increase in the amount of MAO has improved the productivity and selectivity of ethylene to 1-hexene. However, using too much MAO will make the process uneconomic due to its high price.

Pre-alkylation of the catalyst prior to its addition to the reactor was tested by feeding half the MAO to the reactor and stirring it for 5 min; the other half was contacted with the catalyst for 1 min before being added to the reactor. Pre-alkylation of the catalyst increased the productivity of ethylene trimerization (Table 3).

Effects of reaction temperature and pressure

The effects of reaction temperature on productivity and selectivity are shown in Table 4. The catalyst was less activated at 5 °C and below, which reduced productivity. The catalyst suffered from high deactivation rates at 25 °C and

Table 1 Ethylene trimerization with catalysts/MAO system[a]

Catalyst	Cat. amount (μmol)	MAO amount (e.q.)	Temp. (°C)	Pressure (bar)	$C_6 =$ productivity (kgC_6/mmolTi h)	$C_6 =$ selectivity (wt.%)
1[b]	40	1,000	15	7	6.01	90.3
2[b]	40	1,000	15	7	6.55	90.4
3[b]	20	1,000	15	7	5.33	75.0
4[b]	20	1,000	15	7	5.39	86.0
5[b]	20	1,000	15	7	4.35	58.8
6[c]	40	1,000	15	7	4.52	90.5
7[c]	40	1,000	15	7	4.69	89.7
8[c]	20	1,000	15	7	3.82	58.1
9[c]	20	1,000	15	7	3.48	83.3
10[c]	20	1,000	15	7	3.27	74.6

[a] Reaction conditions: toluene solvent, 15 min. reaction time

[b] Cyclopentadienyl-arene titanatrane catalysts

[c] Cyclopentadienyl-arene titanium chloride catalysts

Table 2 Effects of the amount of MAO

Entry	MAO amount (e.q.)	Temp. (°C)	Pressure (bar)	$C_6 =$ productivity (kgC_6/mmolTi.h)	$C_6 =$ selectivity (wt.%)
1	500	20	7	4.16	87.4
2	1,000	20	7	5.98	90.8
3	2,000	20	7	6.36	91.3

Reaction conditions: 40 µmol of Catalyst 1, toluene solvent, 15 min. reaction time

Table 3 Effects of the method of MAO feeding[a]

Entry	MAO amount (e.q.)	Temp. (°C)	Pressure (bar)	$C_6 =$ productivity (kgC_6/mmolTi h)	$C_6 =$ selectivity (wt.%)
1	1,500	20	7	6.61	92.8
2[b]	1,500	20	7	7.98	92.1

[a] Reaction conditions: 40 µmol of Catalyst 2, toluene solvent, 15 min. reaction time

[b] Half of the MAO was pre-contacted with catalyst and half of the MAO was fed to the reactor

Table 4 Effect of the reaction temperature

Entry	MAO amount (e.q.)	Temp. (°C)	Pressure (bar)	$C_6 =$ productivity (kgC_6/mmolTi h)	$C_6 =$ selectivity (wt.%)
1	1,000	5	7	2.22	48.2
2	1,000	10	7	5.72	84.5
3	1,000	15	7	6.55	90.4
4	1,000	20	7	6.57	92
5	1,000	25	7	3.80	77
6	2,000	30	10	0.55	39

Reaction conditions: 40 µmol of Catalyst 2, toluene solvent, 15 min. reaction time

Table 5 Effect of the reaction pressure

Entry	MAO amount (e.q.)	Temp. (°C)	Pressure (bar)	$C_6 =$ Productivity (kgC_6/mmolTi h)	$C_6 =$ Selectivity (wt.%)
1	1,000	20	7	6.57	92
2	1,000	20	10	10.3	92.3

Reaction conditions: 40 µmol of Catalyst 2, toluene solvent, 15 min. reaction time

above, which significantly reduced 1-hexene productivity and selectivity. Operation was optimized at 10–20 °C.

As shown in Table 5, the reaction pressure also had a clear effect on the productivity of 1-hexene, which increased with increasing pressure. Selectivity was not greatly affected by pressure changes. The rate of ethylene conversion by this type of catalyst was approximately first order relative to ethylene concentration, similar to Hessen et al.'s catalyst [9].

These results suggest that the reaction's temperature and pressure can be optimized for production of 1-hexene, which was produced by this catalyst system at a moderate temperature and pressure compared with a conventional chromium catalyst (100–130 °C and 50–100 bar) [19–21]. Therefore, this catalyst system could afford energy savings.

Conclusions

The selective trimerization of ethylene was investigated using catalytic systems containing potentially tetradentate trianionic triethoxyamine. The catalysts showed selective ethylene trimerization (92.3 wt.%) with good 1-hexene productivity (10.3 kgC_6/mmolTi h). Small amounts of polyethylene byproduct were also produced.

Pre-alkylation of the catalyst with MAO increased the productivity of ethylene trimerization. Ethylene conversion was approximately first order with respect to ethylene concentration. 1-Hexene was produced under moderate reaction conditions that required less energy to maintain than other systems. Structural analysis of these compounds is underway.

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