OLIGOMERISATION OF OLEFINIC COMPOUNDS WITH REDUCED POLYMER FORMATION

TECHNICAL FIELD

This invention relates to the oligomerisation of olefinic compounds in the presence of an activated oligomerisation catalyst and relates further to the use of a non-metal oxygen containing additive in oligomerisation.

BACKGROUND OF THE INVENTION

A number of different oligomerisation technologies are known to produce α-olefins. Some of these processes, including the Shell Higher Olefins Process and Ziegler-type technologies, have been summarized in WO 04/056479 A1. The same document also discloses that the prior art (e.g. WO 03/053891 and WO 02/04119) teaches that chromium based catalysts containing heteroaromatic ligands with both phosphorus and nitrogen heteroatoms, selectively catalyse the trimerisation of ethylene to 1-hexene.

US Pat No. 4,540,755 discloses polymerisation of olefins. WO2009/108174 A1 discloses modified chromium-based catalysts and polymerisation processes for using same.

Processes wherein transition metals and heteroaromatic ligands are combined to form catalysts for trimerisation, tetramerisation, oligomerisation and polymerisation of olefinic compounds have also been described in different patent applications such as WO 03/053890 A1; WO 03/053891; WO 04/056479 A1; WO 04/056477 A1; WO 04/056480 A1; WO 04/056478 A1; WO 05/123884 A2; WO 05/123633 A1 and US Pat No. 7,285,607.

The catalysts utilized in the abovementioned trimerisation, tetramerisation, oligomerisation or polymerisation processes all include one or more activators to activate the catalyst. Suitable activators include

Table 9: Effect of dioxygen upon batch operation tetramerisation catalysis with the triethylaluminium–*tetrakis*(perfluorophenyl)borate catalyst – addition of pure dioxygen gas to reactor headspace. Pure oxygen gas was injected into the reactor headspace via syringe.

Entry	Cr {μmol}	O_2 addition {cm^3}	(mol O_2) (mol Cr)$^{-1}$ (10^6 Prod)$^{-1}$	Productivity {g/gCr}	Activity {g/gCr/h}	C_6 (1-C_6) {wt%}	C_8 (1-C_8) {wt%}	C_{10-15} {wt%}	PE {wt%}
T9-1	2.5	0.01	0.52	255,478	412,779	30.4 (91.9)	53.1 (99.6)	6.0	10.2
T9-2	2.5	0.5	8.6	962,377	4,914,265	33.3 (90.7)	56.7 (99.5)	9.5	0.3
T9-3	2.5	0.5	8.8	943,331	4,851,417	33.3 (91.0)	57.1 (99.5)	8.8	0.6
T9-4	2.5	3.0	170.6	292,632	877,896	40.7 (95.4)	40.1 (99.7)	5.0	14.3

General conditions: $Cr(acac)_3$; 1.2eq *bis*(diphenylphosphanyl)(isopropyl)amine; 2.4 eq $[Ph_3C][B(Ph^F)_4]$; 150 eq $AlEt_3$; 50 bar ethene; 60°C; 100 mL PhCl; 450 mL autoclave.

CLAIMS

1. A process for producing an oligomeric product by oligomerisation of at least one olefinic compound, the process including:

a) providing an activated oligomerisation catalyst by combining, in any order,

i) a source of chromium;

ii) a ligating compound of the formula

$$(R^1)_m X^1 (Y) X^2 (R^2)_n$$

wherein X^1 and X^2 are independently an atom selected from the group consisting of nitrogen, phosphorus, and oxygen or an oxidised nitrogen or phosphorus atom where the valence of X^1 and/or X^2 allows for such oxidation;

Y is a linking group between X^1 and X^2;

m and n are independently 0, 1 or a larger integer; and

R^1 and R^2 are independently hydrogen, a hydrocarbyl group, an organoheteryl group, a heterohydrocarbyl group, a substituted hydrocarbyl group, or a substituted heterohydrocarbyl group, and R^1 being the same or different when m>1, and R^2 being the same or different when n>1; and

iii) a catalyst activator or combination of catalyst activators; and

b) contacting at least one olefinic compound with the activated oligomerisation catalyst in the presence of a non-metal oxygen containing additive, which non-metal oxygen containing additive may be introduced together with the activated catalyst, after introduction of the activated catalyst but prior to introduction of the olefinic compound, together with the olefinic compound, or after the olefinic compound has contacted the activated catalyst, the non-metal oxygen containing additive being present in an amount such that the ratio of the molar amount of the non-metal oxygen containing additive to the molar amount of chromium per 10^6 g/g Cr productivity in the source of chromium is between 0.01 and 400.

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