Ethylene Oligomerisation with Zirconium Arylalkyls and Alkenyls

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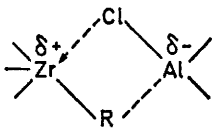
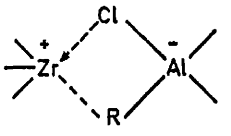
Summary The addition of alkylchloroaluminium derivatives to ZrR_4 (R = allyl or benzyl) produces active catalysts for the preparation of C_4—C_{20} α-olefins from ethylene.

Bestian and Clauss[1] used the soluble catalyst, $MeTiCl_3 \cdot MeAlCl_2$ at low temperatures to oligomerise ethylene to predominantly 2-ethyl-α-olefins. More recently, Langer[2] has used $TiCl_4 \cdot Et_nAlCl_{3-n}$ and obtained high proportions of linear α-olefins. Similar results have been patented[3] for

$Zr(OR)_4 \cdot R_nAlCl_{3-n}$ catalysts. In contrast, it is known that $Zr(CH_2{:}CH{\cdot}CH_2)_4$ and $Zr(PhCH_2)_4$[4,5] catalysts in homogeneous solution produce high polymer from ethylene.



(I)



(II)

We now find that a combination of $Zr(PhCH_2)_4$ or $Zr(CH_2{:}CH{\cdot}CH_2)_4$ with alkylchloroaluminium gives a catalyst, which forms very little polymer, but produces linear α-olefins in the C_4—C_{20} range with an activity significantly higher than is reported[1–3] for the other oligomerisation catalysts. Experiments were performed in toluene solution at 40—80° with ethylene pressures up to 11 kg cm^{-2} (see Table). The product from these reactions is essentially pure α-olefin as determined by i.r. and n.m.r. spectroscopy. The proportion of product of chain length $>C_{20}$ is usually not more than 5%; the first experiment in the Table gave 2 g insoluble polymer and 83 g of distilled C_4—C_{20} oligomers in a reaction time of 30 min. In a typical case, g.l.c. analysis gave well separated peaks, corresponding to oligomers in the sequence C_4 (11·8)† C_6 (14·8), C_8 (16), C_{10} (14·3), C_{12} (9·8), C_{14} (9·2), C_{16} (7·0), C_{18} (5·8), C_{20} (4·1), C_{22} (2·3), $>C_{22}$ (4·6). The formation of such high proportions of oligomers was unexpected, although Giannini *et al.*[5] had noticed the formation of some low molecular weight oligomers when using freshly prepared solutions of the polymerisation catalyst $Ti(PhCH_2)_4$, $Al(PhCH_2)_3$.

Table

Catalysed oligomerisation of ethylene[a]

Catalyst (mmol)	Co-catalyst (mmol)	Temp. (°C)	Pressure[b] (kg cm^{-2})	Activity[c]
$Zr(PhCH_2)_4$ (0·25)	$Et_3Al_2Cl_3$ (1·0)	40	11	62
" (1·0)	" (4·0)	80	11	61
" "	"	40	6	37
" "	"	40	2	51
" "	$EtAlCl_2$ (4·0)	40	6	28
" "	$Me_3Al_2Cl_3$ (4·0)	80	11	19
$Zr(CH_2{:}CH{\cdot}CH_2)_4$	$Et_3Al_2Cl_3$ (1·0)	80	11	28
" (1·0)	"	40	11	18

[a] All reactions were carried out in toluene (500 ml) in a steel autoclave (1 l). [b] An approximately constant pressure was maintained, by periodically opening a valve to a high pressure ethylene source. [c] Expressed as g product/mmol catalyst/kg cm^{-2} of C_2H_4.

Experiments with a number of aluminium alkyl co-catalysts showed that the best activities were obtained for $Zr(PhCH_2)_4 \cdot Et_3Al_2Cl_3$; the order of activity with different aluminium species was $Et_3Al_2Cl_3 > EtAlCl_2 > Me_3Al_2Cl_3 > Et_2AlCl$.

The very large increase in activity (10^2—10^3) for these catalysts relative to that of the simple transition-metal arylalkyl or alkenyl in polymerisation (0·1 g/mmol/kg cm^{-2}/h for benzyl;[5] 2 g/mmol/kg cm^{-2}/h for allyl[6]) provides direct evidence that the role of aluminium alkyls in Ziegler systems is not merely that of a simple alkylating agent. It is probable that the aluminium component enhances activity by increasing the positive charge at zirconium by successive replacement of allyl or benzyl substituents by chlorine‡ and by the formation of polar binuclear species such as (I) and (II).

Similarly the decrease in molecular weight by a factor of 10^3—10^4 on introducing aluminium alkyls suggests that increasing the positive charge at zirconium has an even greater effect on the rate of termination, increasing it by a factor of *ca.* 10^5—10^6. It is possible that such a dramatic change could be caused by transfer of the growing chain onto the aluminium (II where R = growing chain).

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† Figures in parentheses give the wt. % of each component.

‡ *I.e.* the reverse of the conventional alkylation in a Ziegler catalyst.

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