工業技術研究院
Industrial Technology
Research Institute

聚烯烴系列潛力產品座談會

Linear α-olefin技術發展及潛力應用

時國誠

工業技術研究院 材料與化工研究所

中華民國 106年 02 月 24 日

Background

- Linear Alpha Olefins (LAOs, even-carbon numbered olefins ranging from C4 to $C30^{+}$ carbon atoms.
- The main applications for the LAOs are as co-monomers for polyethylene production, for oxo-alcohols used in detergent and plasticizers and for the production of poly-alpha olefins for the synthetic lubricant pool.
- The total world production for LAOs accounted for 3.5 Mt/y in 2012 for a total capacity of 4.3 Mt/y (with the exception of 1-butene production from refinery streams). The global annual average growth for LAOs is estimated at 3.3% (2012-2018) but depends largely on the region with a higher growth in developing countries.
- Globally, co-monomer grade LAO consumption (C4-C8) is the largest and fastest-growing application, particularly for the production of linear low-density polyethylene resins (LLDPE).

LAOs by ethylene oligomerization processes

full-range processes-technology and market survey

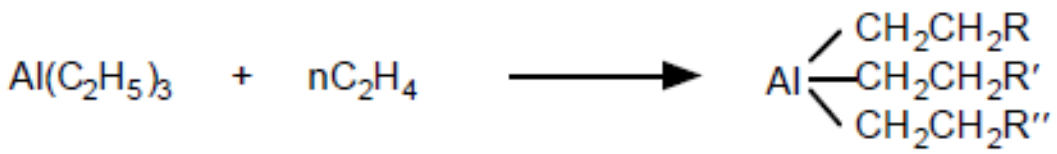
Company (industrial)	Type of catalyst	Typical LAO distribution (wt. %)	World capacity (2012, kt/y)	Announced new capacities (> 2012, kt/y)
CPChem	$AlEt_3$ (1 step)	C_4-C_{10} = 54 (49) [(a)] C_{12}-C_{14} = 18 (18) C_{16}-C_{20+} = 28 (33)	1053	140
Ineos	$AlEt_3$ (2 steps)	C_4-C_{10} = 70-77 C_{12}-C_{14} = 21-28 C_{16}-C_{20+} = 2	565	375
Shell	Ni/P-O (biphasic)	C_4-C_{10} = 54 (32) [(a),(b)] C_{12}-C_{14} =18 (16) C_{16}-C_{20+} =28 (52)	1251	650
Idemitsu	$Zr/L/AlR_{3-x}Cl_x$ (solvent)	Non disclosed	60	330
SABIC/Linde	$Zr/L/AlR_{3-x}Cl_x$ (solvent)	C_4-C_{10} = 82 (26) [(a)] C_{12}-C_{20+} = 18 (74)	250	37

(a) Typical distribution, in brackets possible flexibility (b) possible distribution of LAOs after oligomerization and before isomerization and metathesis processing

Source: IHS Chemicals, Chemical Economies Handbook:Linear alpha-Oiefins, August 2013.

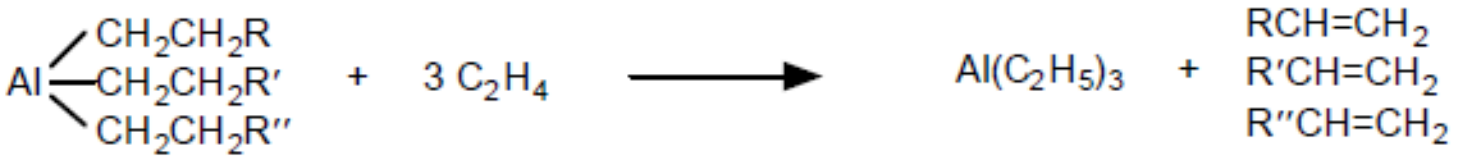
Zieglar processes-CPChem

Growth



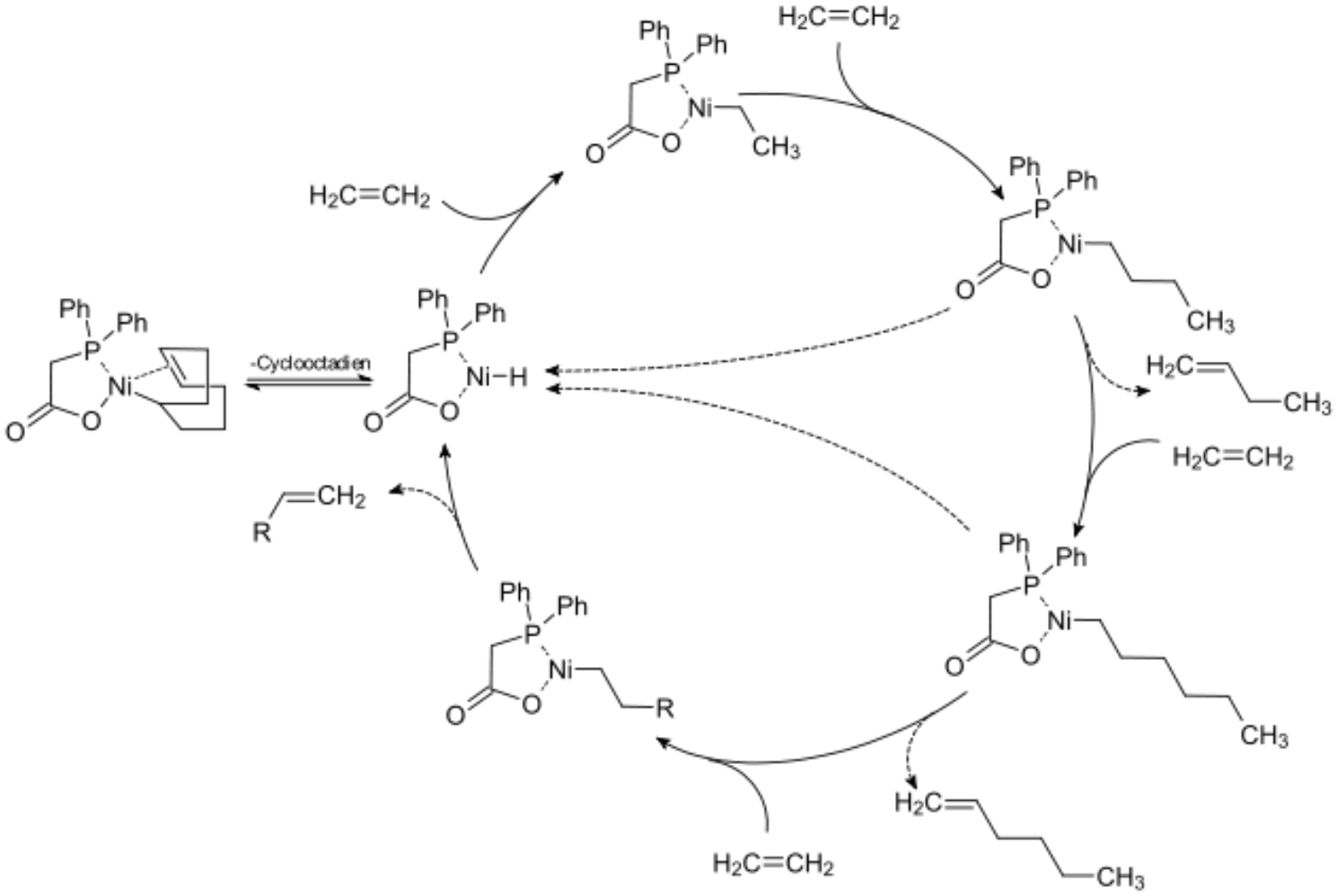
triethylaluminum ethylene growth product

Displacement



growth product ethylene triethylaluminum **alpha-olefins**

SHOP processes-CPChem



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LAOs by ethylene oligomerization processes

On purpose processes[(a)] for the selective production of 1-butene, 1-hexene and 1-octane

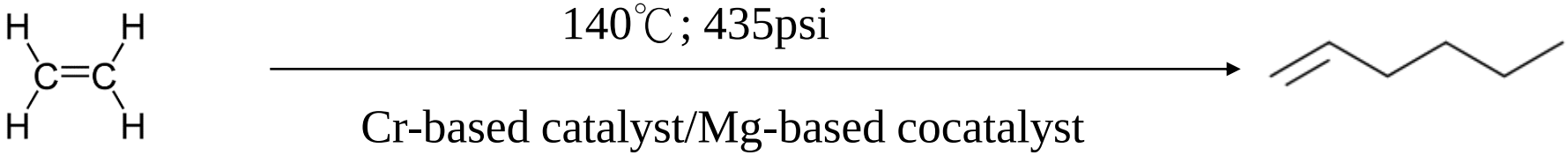
LAO produced	Process/company	Catalyst type	Capacity (kt/y) [(b)]
1-Butene	AlphaButol /Axens	Ti/AlR_3	708
1-Hexene	CPChem	Cr proprietary/ AlR_3	397
1-Hexene	AlphaHexol/Axens	Cr proprietary /AlR_3	50 [(c)]
1-Hexene	Mitsui	Ti proprietary /"MAO"	30
1-Octene/1-Hexene	Sasol	Cr proprietary/ "MAO"	100

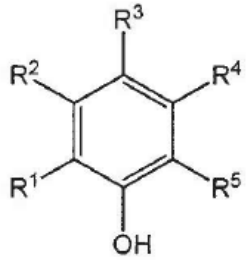
(a) only commercialized processes are cited here (b) include planned capacities (c) total capacity for 2 units AlphaButol et AlphaHexol

Source: IHS Chemicals, Chemical Economies Handbook:Linear alpha-Oiefins, August 2013.

- The first AlphaHexol unit was commercialized in 2012.

AlphaHexol/Axens

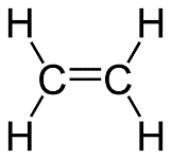




Ligand precursor

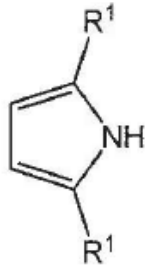
- The reaction yield of C6 olefins is over 85% with some C4 as well as higher carbon number olefins as by-products.
- The selectivity of the alpha-olefins in the C6 fraction is very high, at over 99%
- The first AlphaHexol unit was commercialized in 2012.
- PEP Review 2012-11

Ethylene trimerization processes-Chevron Phillips



Cr(III) 2-ethylhexanoate/2,5-dimethylpyrrole
Triethylaluminum/diethylaluminum chloride

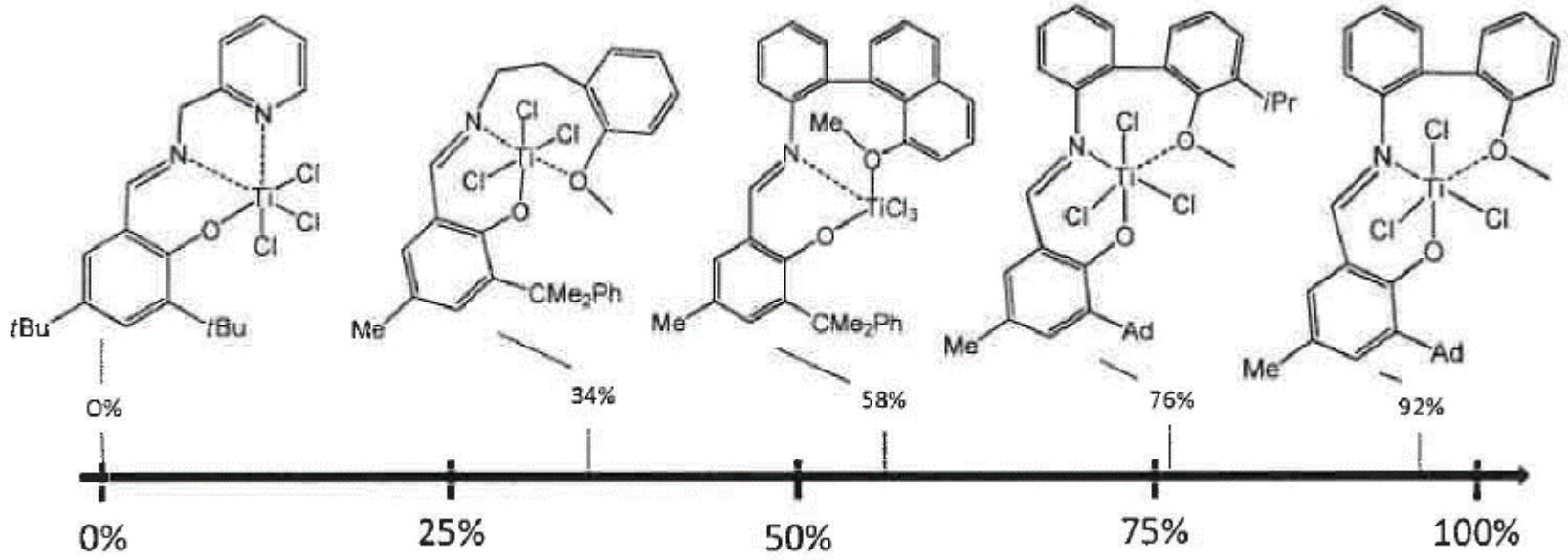
110-130℃; 700-800psi



Ligand precursor

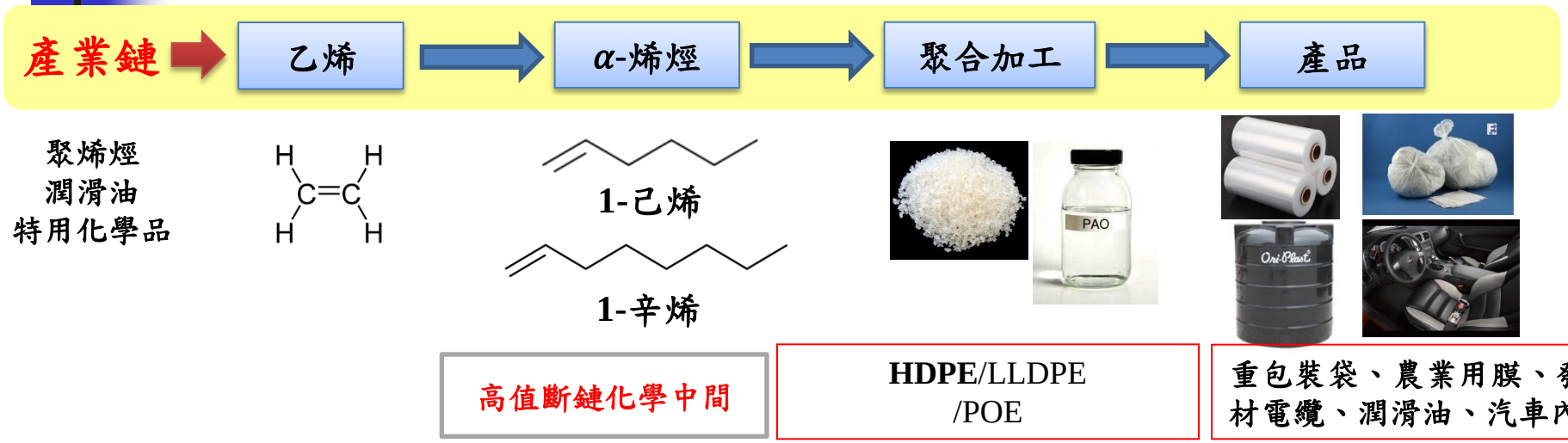
- LP (CPChem) reported the use of pyrrolide ligand in 1991.
- CPChem implemented this technology through two joint ventures with Qatar Chemical Company Ltd. in Mesaieed (Qatar) and Saudi Polymers Company in Al Jubail (Saudi Arabia), producing 47000 t/y and 100000 t/y, respectively. ln 2014, CPChem also announced the start-up of a 1-hexene production unit of 250000 t/y in Baytown, Texas (USA).

Ethylene Trimerization Processes-Mitsui



% wt of 1-hexene in the products distribution

聚烯烴新料源開發(C6/C8 α-olefin)



- 長鏈端烯烴(*α-olefin*)中1-己烯和1-辛烯，是生產LLDPE和HDPE中重要的共聚單體，為我國斷鏈原料。使用長鏈端烯烴的中游產品C6、C8-LLDPE具有拉伸強度高、抗衝擊和抗撕裂等優點，耐環境應力開裂性能可達5000h以上，其特別適合於生產包裝膜和農用薄膜，國內尚未生產此規格產品，依賴進口。
- 長鏈端烯烴也是製造聚烯烴彈性體(POE)以及合成潤滑油等產品的重要原料。