

Oligomerization of α -Olefins to Higher Oligomers

JADWIGA SKUPIŃSKA

Department of Chemistry, Warsaw University, ul. Pasteura 1, 02-093 Warszawa, Poland

Received August 30, 1990 (Revised Manuscript Received February 12, 1991)

Contents

Abbreviations	613
I. Introduction	613
II. Principles of Oligomerization Reactions	614
III. Ethylene Oligomerization	614
III.1. Transition-Metal Complexes as Catalysts for Ethylene Oligomerization	614
III.1.1. Titanium	614
III.1.2. Zirconium	617
III.1.3. Nickel	624
III.1.4. Other Metals	626
III.2. Aluminum	626
III.3. Inorganic Heterogeneous Catalysts of Ethylene Oligomerization	627
III.4. Industrial Ethylene Oligomerization Processes	627
IV. Oligomerization of Propylene	629
IV.1. Transition-Metal Complexes as Catalysts of Propylene Oligomerization	629
IV.1.1. Titanium	629
IV.1.2. Zirconium	629
IV.1.3. Nickel	633
IV.1.4. Various Metals	634
IV.2. Cationic Oligomerization of Propylene	634
V. Oligomerization of Higher α -Olefins	635
V.1. Organometallic Complexes as Catalysts of Higher α -Olefin Oligomerization	635
V.1.1. Titanium and Zirconium	635
V.1.2. Nickel	640
V.1.3. Tungsten	641
V.1.4. Aluminum	641
V.2. Lewis and Brønsted Acids as Catalysts	641
V.3. Inorganic Oxides	642
VI. Conclusions	642
VII. References	642

Abbreviations

Cy	cyclohexyl
Cp	cyclopentadienyl
COD	cyclooctadiene
acac	acetylacetonato (2,4-pentanedionato)
sacsac	2,4-pentanedithionato
P^{O}	bifunctional phosphine
PE	polyethylene
PP	polypropylene
EPR	electron paramagnetic resonance

I. Introduction

Olefins, particularly ethylene, propylene, and butenes, are the basic building block of the petrochemical in-

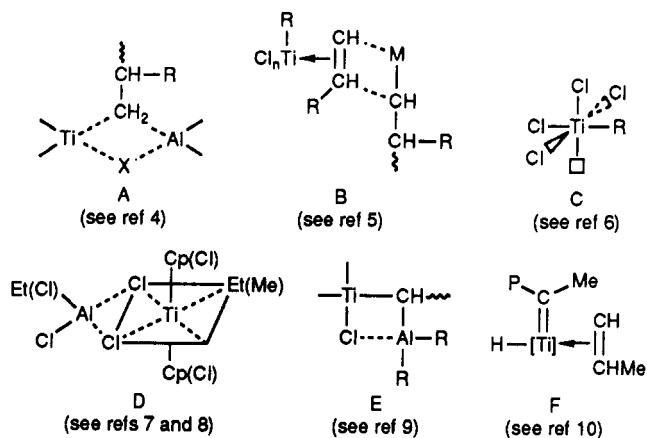
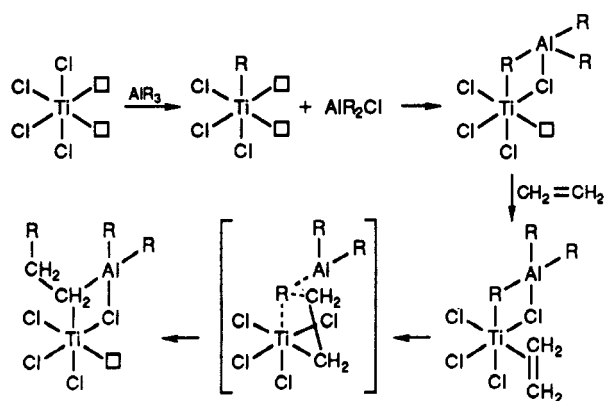


Jadwiga Skupińska was born in Poland and obtained a M.Sc. degree in chemistry from Warsaw University of Technology (Poli-technika) in 1970, working on the reaction of organoaluminum compounds with benzonitrile for her diploma. The copolymerization of carbon dioxide with propylene oxide in the presence of organozinc catalysts was the subject of her Ph.L. work which she finished at 1975 also at Warsaw University of Technology. Since 1976 she has been working as a tutor at the Faculty of Chemistry of Warsaw University. Her current interests are chemical technology, homogeneous catalysis, and metalloorganic chemistry.

dustry. They are easily available, cheap, reactive, and readily transferable into a range of useful products. The last 20 years have witnessed increasing importance of higher linear C_{6-20} α -olefins which are today a source of biodegradable detergents, new kinds of polymers, lubricants, and many other industrially useful chemicals.

α -Olefins are obtained generally through the following processes: thermal and catalytical cracking of paraffins, oligomerization of ethylene, dehydrogenation of paraffins, dimerization and metathesis of olefins, dehydration of alcohols, and electrolysis of C_{3-30} straight-chain carboxylic acids. Of this group the first two are commonly used—first for C_{2-5} olefins and the second for higher C_{9-30} α -olefins manufactured in large scale. This last process has recently become an area of theoretical and technological investigations.¹⁻³

In this review, based on the literature up to December 1989, an attempt has been made to present a comprehensive study of the catalyst and the process for ethylene, propylene, and higher olefins oligomerization. The literature data are divided into three parts: ethylene oligomerization, propylene oligomerization, and higher olefins oligomerization. In every part the following catalysts used in these reactions are described: transition-metal complexes, organoaluminum compounds, Lewis and Brønsted type compounds, and inorganic salts and oxides. Also, the olefin oligomerization mechanism in the presence of these catalysts is discussed. The most important oligomerization reactions involves the use of transition-metal complexes as catalysts and, therefore, form the main subject of this

SCHEME I. Bi- and Monometallic Types of Active Centra Proposed for the Ziegler-Natta Catalysts⁴⁷**SCHEME II. Bimetallic Mechanism of Ethylene Oligomerization According to Rodriguez and Looy¹¹**

paper. The industrial processes used in olefin oligomerization are also described at the end.

II. Principles of Oligomerization Reactions

Polyolefin chain formation depending on a number of n reacting molecules is named as follows:¹ dimerization when $n = 2$; oligomerization when $2 > n > 100$; and polymerization when $n > 100$.

The most desirable ethylene oligomerization products are those for which $n \leq 20$. This reaction occurs only in the presence of catalysts. Catalytic cycle of this reaction consists of two steps, the first, the chain growth (propagation) step:



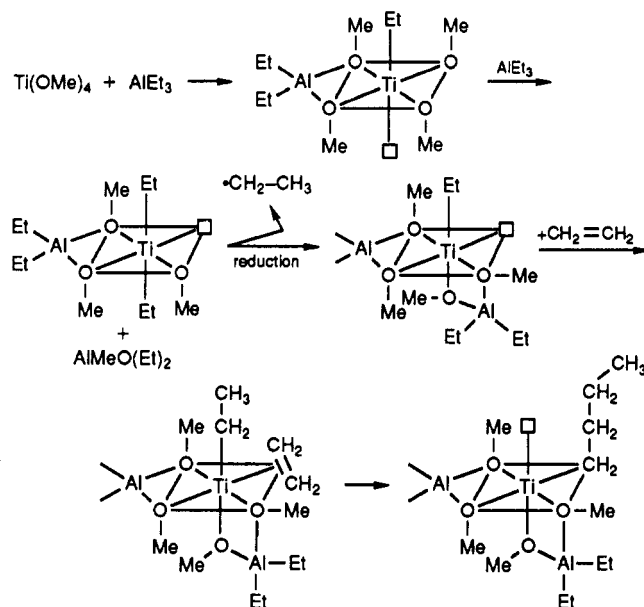
where Cat stands for catalyst; R, alkyl or hydrogen; r_p , propagation rate.

The second step is the hydrogen elimination from β -carbon to the catalytic center:²



where r_t equals chain-transfer rate.

Depending on the catalyst, β -elimination of the hydride occurs when a metal-hydrogen bond is restored, or of a proton, when an acidic center is formed again. The relative reaction 1 and 2 rates, r_p and r_t , respectively, determines the molecular weight of the obtained

SCHEME III. Novaro-Chow-Magnouat Bimetallic Mechanism of Ethylene Oligomerization¹²

product. If $r_p > r_t$, many propagation steps begin before the β -hydrogen transfer occurs and a high molecular weight polymer is formed, when $r_t > r_p$ dimers are obtained, and finally when $r_t \approx r_p$ oligomers are produced. Many factors determine the ratio of the propagation to the chain transfer rate and thereby the molecular weight of oligomerization products. These factors are kind of metal and its oxidation state; electronic properties and steric volume of the ligands attached to metal; reaction temperature and pressure; monomer concentration; and nature of solvent and molecular weight moderators. The influence of these factors on olefin oligomerization will be discussed in the following sections.

III. Ethylene Oligomerization

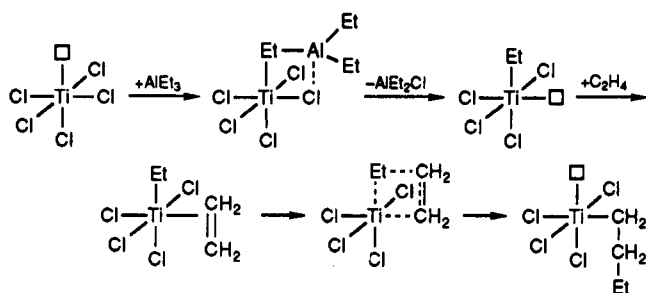
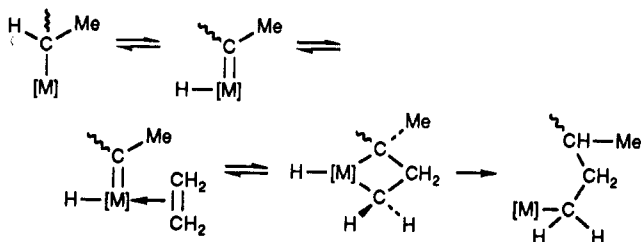
Depending on the mechanism of catalyst action the catalysts are divided into the following classifications: transition-metal complexes in homogenous and heterogeneous systems; organoaluminum compounds; and inorganic salts and oxides.

III.1. Transition-Metal Complexes as Catalysts for Ethylene Oligomerization

Complexes of titanium and nickel are the most often used catalysts for ethylene oligomerization. Zirconium complexes have also been found to be very active catalyst in this reaction.¹⁻³ The use of other transition-metal complexes in ethylene oligomerization is very rare. In catalytic reactions by transition-metal complexes obtained ethylene oligomers follow a Schulz-Flory type distribution.^{24,17,55}

III.1.1. Titanium

Chloro and alkoxy derivatives of titanium modified with organoaluminum compounds—particularly with chloroalkylaluminum one—are active in ethylene oligomerization. This reaction takes place via the following steps: active center formation, olefin coordination

SCHEME IV. Cossee-Arlman Monometallic Mechanism of Ethylene Oligomer Chain Growth⁶**SCHEME V. Green Monometallic Mechanism of Ethylene Oligomer Chain Growth (Metathesis Type)¹⁰**

on the titanium atom and chain propagation, and termination of the chain growth.

Formation of Titanium Catalytic Center. An unoccupied coordination site and titanium-alkyl bond in the titanium complex are fundamental requirements for its catalytic activity in olefin oligomerization reaction. The titanium-alkyl bond is formed in the reaction of a titanium compound with alkyl or alkylchloroaluminum compounds when e.g. halide atoms or alkoxy groups of titanium compounds are replaced by alkyl groups of aluminum derivatives. There are many proposals concerning the structure of the Ziegler-Natta catalyst active centers. They are presented on Scheme I. They consist of bimetallic systems in which titanium is bonded to aluminum through halide or halide-alkyl bridges or of monometallic systems where only a titanium ion is the catalytic center.

Oligomer Chain Growth. Oligomer chain growth occurs as the result of olefin coordination on a titanium atom and consecutive olefin insertion into a Ti-C bond. Olefin insertion into a titanium-alkyl bond is the fundamental step of the olefin oligomerization reaction in the Ziegler-Natta catalysts. Extensive studies of olefin insertion mechanism support the bimetallic or monometallic models of catalytic centers.

The olefin oligomerization mechanism on bimetallic center proposed by Rodriguez and Looy¹¹ is presented in Schemes II and III for ethylene oligomerization on the $(\text{MeO})_4\text{Ti}/\text{Et}_3\text{Al}$ system.¹² In these two examples, the first step of the reaction is the alkylation of the titanium center. Next ethylene is coordinated to the titanium center. This is the cause of the weakness of Ti-C bond and it in turn helps ethylene to insert into the Ti-C bond. Simultaneously, according to Rodriguez and Looy¹¹ (Scheme II), the Al-C bond is cleaved and the new bridge Al-C-Ti is formed. This way the new active center is regenerated and the catalytic cycle continues.

For the catalytical complex $(\text{MeO})_4\text{Ti}/\text{Et}_3\text{Al}$, presented in Scheme III part a, structure of a trigonal bi-

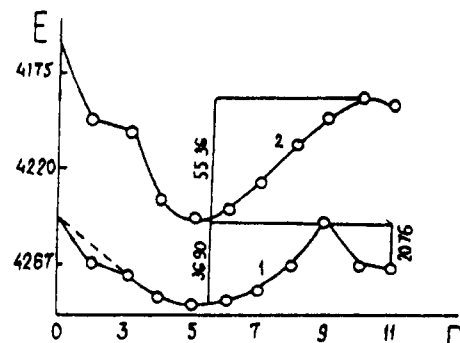


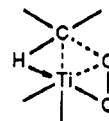
Figure 1. Variation in the energy (E , cal/mol) of the basic state in the course of polymerization ($\text{TiCl}_4/\text{R}_3\text{Al}$):¹⁶ 1, via bimetallic mechanism; 2, via monometallic mechanism.

pyrimid has been proposed. The organoaluminum compound plays a dual role. It exchanges the ligands with the titanium ion thereby forming a labile titanium-alkyl bond and forms, via the Al-O-Ti bridges, the adequately geometrical structure and reduces the titanium(IV) ion to a titanium(III) one. Ethylene complexation causes the change in the complex structure to an octahedra in which ethylene is coordinated and then inserted into the Ti-C bond.

In the case of the monometallic active center three mechanisms are postulated. The first, where olefin insertion occurs via four-center intermediate proposed by Cossee and Arlman,⁶ is presented on Scheme IV. The ethylene oligomerization is initiated here only with the titanium ion and its ligands. Organoaluminum compounds alkylate only the titanium ion. The resulting titanium complex has an octahedral structure with one unoccupied coordination site, which is the active center where ethylene is coordinated at the first step of catalytic cycle.

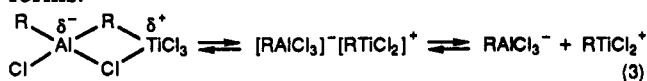
The metathesis type mechanism of olefin oligomerization proposed by Green and Rooney¹⁰ is presented on Scheme V. A metal carbene $\text{Ti}=\text{CHR}$ is the catalyst center here. This is formed as a result of α -hydrogen shift from the growing oligomer chain to the titanium ion.

Recently, Brookhart and Green^{13,14} have proposed a mechanism which is a minor variation of the earlier example. In this mechanism the cleavage of the C-H bond does not occur exactly as in the above model. The "agostic" hydrogen structure is postulated as



Both the mono and bimetallic mechanism are supported by theoretical calculations, the results of which e.g. obtained by Minsker¹⁶ are pictured in Figure 1. These calculations show that the bimetallic mechanism is energetically favorable but the Jolly and Marynick calculations for $\text{Cp}_2\text{TiCH}_3^+$ claim that olefin insertion into the titanium-alkyl bond should occur in the absence of organoaluminum compounds.¹⁵

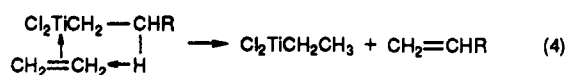
Langer¹⁷ has proposed for the TiCl_4 /alkylchloroaluminum system an ionic structure of three equivalent forms:



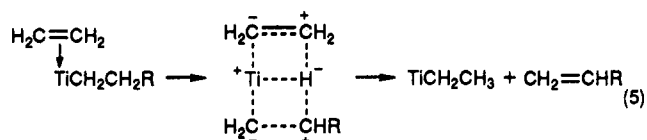
Similar ionic structures have been proposed for the

following systems active in the ethylene oligomerization: $\text{CH}_3\text{TiCl}_3/\text{CH}_3\text{AlCl}_2$ ¹⁸ and $\text{TiCl}_4/\text{R}_{3-n}\text{AlCl}_n$.¹⁹ The influence of the solvents used in this reaction was investigated^{19,20} and the following order of their effect was established: chlorohydrocarbons > toluene > heptane. This implies that the increase of solvent polarity enhances the ethylene oligomerization rate. This observation supports an ionic character of olefin oligomerization catalysts. More detailed investigations²⁵ showed that at relatively low temperatures, from 293 to 313 K, ethylene and propylene cooligomerization occurs according to anionic coordination mechanism, but at temperatures > 353 K, this reaction assumes a cationic character.

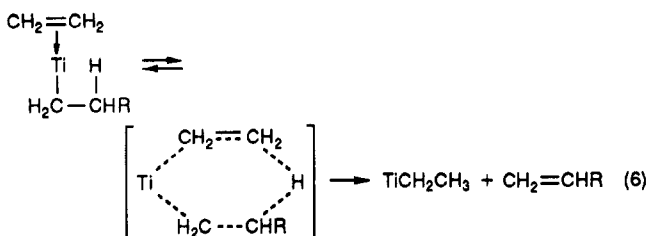
Chain-Transfer Reaction. As mentioned above, the relative rates of chain growth and chain transfer determine the molecular weight of obtained oligomers. This process on the titanium complex catalysts occurs as a result of the β -hydrogen elimination from the oligomer chain to the coordinated olefin²¹ after which the α -olefin oligomer is liberated and the catalytic center, namely, the titanium-alkyl bond is restored.



Investigations of the temperature influence on ethylene oligomerization in presence of $(\text{EtO})_4\text{Ti}/\text{EtAlCl}_2$ system²² show that activation energy of the β -hydrogen elimination (28 kJ/mol) is lower than that of olefin insertion into a Ti-C bond (38.7 kJ/mol). This fact is explained by a six-center intermediate formation during the β -elimination step:



Novaro and co-workers,¹² on the basis of a theoretical analysis of the oligomer chain growth, β -hydrogen transfer, and kinetics of ethylene oligomerization on titanium catalysts, have proposed an alternate six-center intermediate without Ti-H bonds^{2,12,21} for the β -hydrogen-elimination step:



Most data concerns ethylene oligomerization on the $\text{TiCl}_4/\text{Et}_n\text{AlCl}_{3-n}$ systems. The influence of reaction conditions on selectivity, Schulz-Flory molecular weight oligomers distribution and yields has been investigated. These factors are catalyst composition—Ti/Al ratio, catalyst concentration, pressure and temperature, kind of solvent, reaction time, and kind of the titanium and aluminum ligand.

Al/Ti Ratio.^{17,19,23,24} When the ratio $\text{Al/Ti} \leq 1$ the ethylene oligomerization does not occur. At ratios > 2, the catalyst efficiency improves.

Catalyst Concentration.^{23,24} A decrease of catalyst concentration causes an increase of the oligomer chain

transfer rate—more short chain olefins are obtained. Increasing the catalyst concentration gives more polymer; thus, decreasing the reaction selectivity. This polymer formation is a result of cooligomerization of ethylene with oligomers.

Pressure.^{19,23,24} With increase of reaction pressure, the molecular weight of oligomers as well as conversion to linear α -olefins increases. An increase in the ethylene pressure also inhibits the ethylene cooligomerization with higher α -olefins.

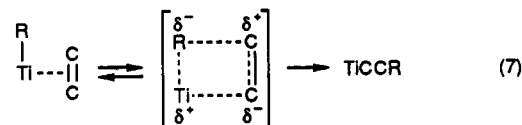
Temperature.^{19,23,24} Increase in the ethylene oligomerization temperature increases the molecular weight of the oligomers and amount of nonlinear α -olefins in the products.

The rise of the molecular weight of the obtained oligomers is in this case a result of higher activation energy of the chain growth compared to the activation energy of the chain transfer to the monomer (β -hydrogen transfer). Under these conditions, ethylene cooligomerizes with the preformed α -olefins resulting in a significant amount of branched hydrocarbons. Also the reduction of Ti(IV) ions to Ti(III) with organoaluminum compounds is accelerated. This, in turn, gives more catalytically active polymerization centers (Ti(III) ions) and therefore more polyethylene in the products. At higher temperatures the ethylene alkylation of solvents is also accelerated.

Solvent.^{20,26,29} Increasing solvent polarity activates titanium catalyst in the ethylene oligomerization and decreases the molecular weight of obtained oligomers.^{17,20} More branched olefins exist in the product in view of the fact that in more polar solvents the cationic character of the catalyst increases.

Reaction Time.^{17,27} Prolonged reaction time leads to an increase in oligomers' yield and an increase in the amount of branched olefins.

Ligands of Titanium and Aluminum. An increase of acidity of organoaluminum compounds causes a decrease of the oligomer molecular weight. When titanium halide (acceptor) ligands in the system $\text{TiX}_4/\text{EtAlCl}_2$ are changed for alkoxy (donor) more polyethylene is obtained in the products.²⁸ Halide ligands, having acceptor properties, polarize Ti-X bonds by giving a positive charge to the titanium ion. This helps the six-center intermediate formation (see reaction 6) and the termination of the oligomer chain, which is a result of strong polarization of neighboring bonds (including the polarization of $\text{C}_\beta\text{-H}$). Donor ligands, on the other hand, decreasing positive charge on a titanium ion, favor the four-center intermediate formation and the olefin insertion into the Ti-C bond according to the equation 7.²

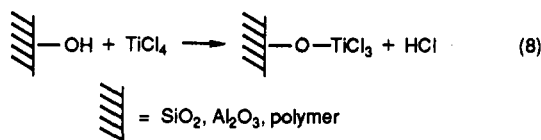


Donor ligands added to the system $\text{TiCl}_4/\text{Et}_n\text{AlCl}_{3-n}$ ($n = 1,2$) increase the catalyst selectivity to linear α -olefins.²⁹ In Table I the catalysts, modified by an addition of ketones, amines, nitriles, phosphines, and sulfur compounds, are presented. With the use of these catalysts the 70–80% yields of C_{8-20} olefins, with selectivity to linear α -olefins equal to 90%, were obtained.

Very high yields have been also obtained for the system $[(\text{C}_6\text{H}_5\text{O})_2\text{PS}_2]_2\text{TiCl}_2/\text{EtAlCl}_2$, 1875 g of oligomer

(g of Ti) $^{-1}$ h $^{-1}$ with a selectivity to α -olefins of 75–85%.³⁰ Donor ligands, here, increase electron density around the titanium ion, which in turn allows only ethylene to coordinate on the titanium and therefore inhibit the cooligomerization between higher α -olefins. Large steric effects of these ligands, in addition to electronic influences, are probably responsible for linear olefin formation.²

Heterogenized Titanium Catalysts. Reaction of titanium compounds with surface hydroxyls of inorganic gels and their strong adsorption on the inorganic salts or oxides and their reaction with active functional groups of polymers lead to heterogenized titanium catalysts, which after modification with alkyl metal derivatives, are active in the olefin oligomerization reactions (reaction 8).



In this reaction, the system (η^5 -C₅H₅)₂TiCl₂/polybutadiene/EtAlCl₂ is highly active for more than 1000 h³¹ with stable selectivity to linear α -olefins of 95–97%. This long activity is a result of isolation of active centers when titanium ions are bonded to the polymer chain in such distances that make the titanium ion agglomeration impossible which in homogeneous systems inhibits catalytic activity.³² Since the long-chain olefins, unlike ethylene, cannot easily reach the catalytic centers located in the pores of the polymeric support, only a small amount of branched olefins is formed. In this case the molecular weight distribution does not follow the Schulz–Flory rule. Relatively, less high molecular weight product is obtained, what probably is connected with diffusion effect. In comparison to its homogeneous analogues, this system is less sensitive to air and moisture.

On the other hand, the catalyst, in which silica gel has the following ligands bound to its surface: (C-H)₂S(CH₂)₂OH, CH₂SC₁₀H₇, and (CH₂)₂C(NH₂)NOH and is the carrier of the system TiCl₄/Et₃Al₂Cl₃, shows less activity and selectivity compared to homogeneous catalysts.³³ In this case, blocking of centers by the formed polyethylene is observed. The system with the sulfur-containing ligands is more active than that one with nitrogen. This phenomena is explained by stronger catalyst stabilization effects caused by back-donation of 3d sulfur orbitals.

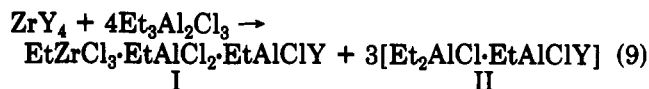
Heterogenous catalysts, namely TiCl₄/EtAlCl₂, supported on carriers with amine groups, (3-amino-propyl)triethoxysilane³⁴ or *p*-(diaminomethyl)styrene³⁵ on their surfaces, show low ethylene oligomerization activity. They give 15–218 g of oligomer (g of Ti) $^{-1}$ h $^{-1}$ with linear olefin selectivity of about 70%.

III.1.2. Zirconium

The systems ZrCl₄, Zr(OOCR)₄, Zr(C₅H₇O₂)₄, and Zr(CH₂C₆H₅)₄ modified with alkylchloroaluminum derivatives are highly active in ethylene oligomerization to long-chain α -olefins.^{36–38} Kinetic investigations of the ethylene oligomerization in presence of the catalyst Zr[OOCCH(CH₃)₂]₄/Et₃Al₂Cl₃ have shown that (1) the oligomerization does not occur when the ratio Al/Zr < 8; (2) the average oligomerization degree (p_n) decreases

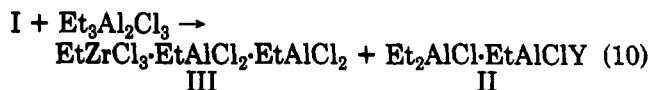
when the ratio Al/Zr increases; and (3) the p_n is not influenced by the kind of the solvent used.

Condition 1—the ratio Al/Zr = 8—is explained by the necessary presence of the four dimeric sesquichloro-sesquiethylaluminum compounds during the oligomerization center formation in the following systems:³⁹



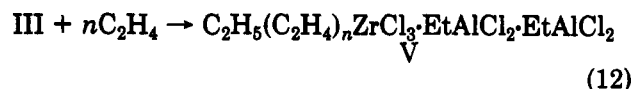
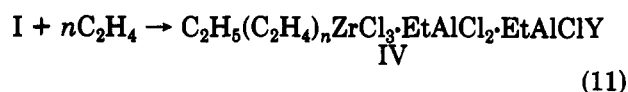
where Y = OOCR, CH₂C₆H₅, C₅H₇O₂.

If an excess of organoaluminum compounds is used, then reaction 10 occurs:

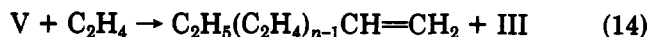
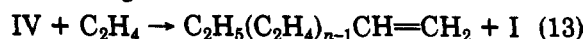


Complexes I and III are the ethylene oligomerization active center. Compound II is inert in ethylene oligomerization.

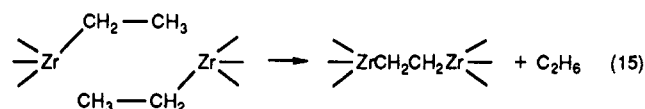
The oligomerization reaction succeeds when ethylene molecules insert into Zr–C bonds in the active complexes I and III.



The oligomer chain termination reaction occurs as a result of the oligomer chain on the monomer transfer.¹³



The rates of cooligomerization reaction, solvent alkylation, and oligomer chain transfer on chloroethylaluminum derivatives were found to be very small. Simultaneously, ethylene oligomerization reaction rate in presence of the above catalysts was observed to decrease with the reaction time. The EPR investigations of the system Zr(*i*-PrCOO)₄/Et₃Al₂Cl₃ have shown that the reduction: Zr(IV) \rightarrow Zr(III) does not occur but reaction 15 takes place.⁴⁰ This disproportionation re-



action is responsible for this catalytic system's deactivation.

Additional information concerning this catalyst's deactivation was obtained from the electrical conductivity investigations in toluene. During oligomerization, ethylene and other α -olefins, were found to form cationic type centers R⁺A⁻ which show little activity under reaction conditions as they dissociate to ions and disappear in subsequent reaction steps. An increase in the solvent's solvating properties in the decreasing order heptane < ligroin < cyclohexane < olefins < toluene increases oligomerization rate modestly but does not change the oligomer molecular weight.⁴⁰

Investigations of the Zr(*i*-PrCOO)₄/Et₃Al₂Cl₃ (Al/Zr = 12) system showed that only 20% of the Zr compound is catalytically active.⁴⁰

TABLE I. Oligomerization of Ethylene

catalyst	react condtn	products	yield	ref(s)
$\text{TiCl}_4/\text{alkylaluminum}$	Titanium			
$\text{TiCl}_4/(\text{C}_2\text{H}_5)_2\text{AlCl}_2/\text{AlCl}_3$ (Al/Ti = 0.5-104)	xylylene, $\text{C}_6\text{H}_6\text{Cl}$, 400 psig, 15-50 °C, 1 h	olefins C_{4-24} = 70%, α -olefins = 56.27% \bar{M}_n olefins = 113-128, linearity = 91.2%	132 g (mmol of Ti) ⁻¹	207
$\text{TiCl}_4/(\text{C}_2\text{H}_5)_2\text{Al}_2\text{Cl}_3$	toluene, 20-25 kg/cm ² , 10 °C, 85 min	olefins C_{6-20} , linearity = 96%		208
$\text{TiCl}_4/(\text{C}_2\text{H}_5)_2\text{Al}_2\text{Cl}_3$ (Al/Ti = 2)	toluene, 2 MPa, 283 K, 1 h	α -olefins = 99%, \bar{M}_n = 138	625 mol of olefins (mol of Ti) ⁻¹ 432 g of product (g of Ti) ⁻¹ 5.3 g of PE 166 g (g of TiCl_4) ⁻¹ h ⁻¹	27, 209
$\text{TiCl}_4/(\text{C}_2\text{H}_5)_2\text{AlCl}_2$ (Al/Ti = 2)	hydrocarbon solvents, 500 psig, 150 °C, 4 h	oligomers, \bar{M}_n = 70-300		17, 210
$\text{TiCl}_4/\text{C}_2\text{H}_5\text{AlCl}_2$ (Al/Ti = 8)	benzene, toluene, 20-80 °C, 15-37 min	\bar{M}_n = 102-189	410 mol of oligomer (mol of Ti) ⁻¹	61
$\text{TiCl}_4/\text{C}_2\text{H}_5\text{AlCl}_2$ (Al/Ti = 8)	benzene, 25 atm, 20 °C, 90 min	\bar{M}_n = 127, α -olefins = 96%	1240 g (g of TiCl_4) ⁻¹ 1.6% PE	19, 23
$\text{TiCl}_4/\text{C}_2\text{H}_5\text{AlCl}_2$ (1:8)	benzene, 6 atm, 40 °C, 88 min	α -olefins = 67.8%, \bar{M}_n = 330	477 mol (mol of Ti) ⁻¹	20
$\text{TiCl}_4/\text{C}_2\text{H}_5\text{AlCl}_2$ (1:4-12)	ethylene chloride, 2.5 atm, -20 °C, 30-100 min	\bar{M}_n = 260-1700	50-248 mol (mol of Ti) ⁻¹	26
$\text{TiCl}_4/\text{C}_2\text{H}_5\text{AlCl}_2$	toluene, 20-25 atm, 20-40 °C 50 psig, 5-25 °C, 1-2 h	olefins C_{12-19} linear α -olefins C_{12-20} = 60-100%, \bar{M}_w = 90-150	ethylene recycling 40-150 g (g of TiCl_4) ⁻¹ h ⁻¹ , traces of PE	83
$\text{TiX}_3/\text{R}_n\text{AlX}_{3-n}$, $\text{TiX}_3\text{OR}/\text{R}_n\text{AlX}_{3-n}$, $\text{TiX}_3\text{OOCR}'/\text{R}_n\text{AlX}_{3-n}$ (Al/Ti = 2-5); n = 1, 2; R and R' = alkyl, X = halogen	50 psig	linear α -olefins C_{12-20} = 97-98%; \bar{M}_n = 110-120	200 g (g of TiCl_4) ⁻¹ h ⁻¹	213
$\text{TiX}_3\text{Y}/(\text{C}_2\text{H}_5)_2\text{AlCl}/\text{MCl}_2$; X = Cl; Y = Cl, OR, OOCR; M = Fe, Sn, B, Ti, Al; R = alkyl	chlorobenzene, xylene, 55-500 psig, -20 °C	linear olefins C_{12-20} = 70-100%	90-147 g (g of TiCl_4) ⁻¹ h ⁻¹	17
$\text{TiCl}_4/(\text{C}_2\text{H}_5)_2\text{AlCl}_2/\text{L}$, L = acetylacetonate (AA), dimethylformamide (DMF), ethylene glycol dimethyl ether (EGE), diethyl ether (DE)	650 psig, 0-50 °C, 1 h	% olefins in product = 30-50, \bar{M}_w = 120, olefins C_{12-30} = 96% olefins $\text{C}_{>30}$ = 23-55%, linearity = 90%	PE = 1%	214
$\text{TiCl}_4/(\text{C}_2\text{H}_5)_2\text{Al}$ or $\text{C}_2\text{H}_5\text{AlCl}_2/\text{ferrocene}/(\text{monochloromethyl})\text{cyclopentane}$ (50:100:16:183 mol)	140 atm, 54 °C	α -olefins C_{18-22} = 36.5% in product	40-272 g of product (g of TiCl_4) ⁻¹ h ⁻¹ , PE = 5-52%, catalytic activity is of the order when L = EGE > DMF > AA > DE	215
$\text{TiCl}_4/\text{C}_2\text{H}_5\text{AlCl}_2/\text{styrene}$ or α -methylstyrene	aromatic solvents 40 atm, 20 °C	\bar{M}_n = 212-220		216
$\text{TiCl}_4/\text{C}_2\text{H}_5\text{AlCl}_2/\text{C}_2\text{H}_5\text{AlCl}_2/\text{L}$ (2:1:6), L = anthracene, menylene, hexamethylbenzene		olefins C_{4-6} = 0.9-6%, C_{6-20} = 76-88% in product, linearity = 69-95%		217
$\text{TiCl}_4/\text{chloroorganaluminums}/\text{L}$ (1:1-10:0.2-2), L = amines, nitriles, ethers, ethylacetate, ketones, diketones		olefins C_{9-20} ≈ 70%, linearity ≈ 90%		218
$\text{TiCl}_4/\text{chloroorganaluminums}/\text{mercaptanes}$, thioethers, amines	-30 to 50 °C	olefins C_6 = 21%, C_{9-20} = 72%, linearity = 96%		219
$\text{TiCl}_4/\text{D}(\text{C}_2\text{H}_5)_2\text{Al}_2\text{Cl}_2/\text{C}_2\text{H}_5\text{AlCl}_2/\text{L}$, D = acetone, acrylonitrile, $(\text{C}_2\text{H}_5)_3\text{P}$; L = ethylmercaptane, Ph_2SO_2 , thiophenol	38.7 kg/cm ² , 20 °C	olefins C_{40-100} olefins C_{9-20} = 90%, linearity = 94%		220
$\text{TiCl}_4/\text{C}_2\text{H}_5\text{AlCl}_2/(\text{C}_2\text{H}_5)_2\text{AlCl}/\text{Bu}_3\text{P}$ (1:1:0.5:100)				221
$\text{TiCl}_4/\text{R}_n\text{AlX}_{3-n}/\text{PX}_3$, X = Ph, alkyl; n = 1, 2				224, 225

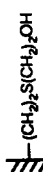
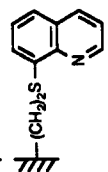
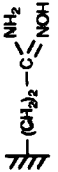
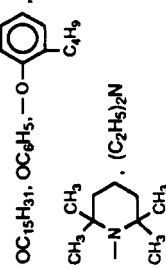
$\text{TiCl}_4/\text{C}_2\text{H}_5\text{AlCl}_2/\text{PCl}_5$	toluene, 450 psig, -5 to 20 °C	olefins $\text{C}_{4-20} = 92-97\%$, linearity = 90%, $\bar{M}_n = 119$	223
$\text{TiCl}_4\text{-R}_3\text{C}^+/\text{C}_2\text{H}_5\text{Al}_2\text{Cl}_3$ (1:0.5-50), R_3C^+ = carbonium salt ($\text{C}_2\text{H}_5\text{O}$) $_2\text{TiCl}/\text{C}_2\text{H}_5\text{AlCl}_2$ (1:5)	toluene, 12 atm, -20 to 0 °C, 1 h	olefins $\text{C}_9 = 32\%$ (α -olefins = 90%), $\text{C}_{10-60} = 67.1\%$ (α -olefins = 85%), $\bar{M}_n = 153$ olefins $\text{C}_4 = 73\%$, $\text{C}_6 = 26\%$, α -olefins = 100%	226 22, 228
$(\text{CH}_3\text{O})_4\text{Ti}/(\text{C}_2\text{H}_5)_3\text{Al}$	12 kg/cm 2 , 40 °C	olefins $\text{C}_4 = 77.6\%$, $\text{C}_6 = 22.0\%$, PE = 0.4%	12 444
$(\text{BuO})_4\text{Ti}/(\text{C}_2\text{H}_5)_3\text{Al}$	<i>n</i> -heptane, H_2 , and C_2H_6 mixture, 2.5 atm, 57 °C, 1 h	olefins $\text{C}_4 = 77.6\%$, $\text{C}_6 = 22.0\%$, PE = 0.4%	444
$\text{TiCl}_4\text{Y}_n/\text{R}_n\text{AlCl}_{3-n}$ (Al/Ti = 23.5-125), $\alpha = 1-2$; R = C_2H_5 , C_4H_9 ; $n = 0-3$; $m = 1-4$; Y = (A) $_2\text{NC}(=\text{S})\text{S}$ -, AOC(=S)S-, (AO) $_2\text{P}(=\text{S})\text{S}$ -, A = C_2H_5 , C_3H_7 , C_4H_9 , C_6H_5	aliphatic or aromatic hydrocarbons, 10-35 atm, -10 to 80 °C	paraffins = 5-13%, olefins = 77-90% (α -olefins = 75-87%), $\text{C}_{6-8} = 20-30\%$, $\text{C}_{12-22} = 27-55\%$, $\text{C}_{>24} = 10-35\%$	30
$\text{TiX}_4/\text{C}_2\text{H}_5\text{AlCl}_2/\text{MY}_n/\text{MgZ}_m$ (1:15-100:0.1-10:0.5-10), X = Cl, Br, acac; $n = 2, 3$; M = Ni, Co, Fe, Cu, Cd, Ca, Zn, Mg; Y = $\text{A}_2\text{NC}(=\text{S})\text{S}$ -, AOC(=S)S-, (AO) $_2\text{P}(=\text{S})\text{S}$ -, A = C_2H_5 , C_3H_7 , C_4H_9 , C_6H_5 ; Z = Cl, SO_2 ; $m = 1, 2$	hydrocarbon solvents, 5-50 atm, 0-80 °C, 1 h	olefins C_{4-40} : $\text{CH}_2=\text{CH}- = 28-35\%$, $-\text{CH}=\text{CH}- = 30-70\%$, $-\text{C}=\text{CH}- = 1-40\%$, $\bar{M}_n = 56-560$ olefins $\text{C}_{4-18} = 17-59\%$; linearity = 57-85%	227
TiCl_4 (surface ligands) / (C_2H_5) $_2\text{Al}_2\text{Cl}_3$ (Al/Ti = 2-3), surface ligands =   	heptane, 30 atm, -10 to 5 °C	olefins $\text{C}_{4-18} = 55\%$, $\text{C}_{>18} = 25\%$ olefins $\text{C}_{4-18} = 59\%$, linearity = 70% olefins C_{4-18} ($\text{C}_{8-18} = 50\%$), linearity = 50%	34 35 31
TiCl_4 supported on borosilicate modified with (aminoalkyl)alkoxysilane/ $\text{C}_2\text{H}_5\text{AlCl}_2$ (Al/Ti = 10)	heptane, 35 atm, -8 °C	olefins $\text{C}_{4-18} = 55\%$, $\text{C}_{>18} = 25\%$ olefins $\text{C}_{4-18} = 59\%$, linearity = 70% olefins C_{4-18} ($\text{C}_{8-18} = 50\%$), linearity = 50%	34 35 31
TiCl_4 attached to graft polystyrene/ <i>p</i> -(diaminomethyl)polystyrene/ $\text{C}_2\text{H}_5\text{AlCl}_2$ (C_2H_5) $_2\text{TiCl}_2$ supported on 1,2-polybutadiene/ $\text{C}_2\text{H}_5\text{AlCl}_2$ (Al/Ti = 8-20)	10 atm, 7 °C heptane, 0.4-2.1	olefins $\text{C}_{4-18} = 55\%$, $\text{C}_{>18} = 25\%$ olefins $\text{C}_{4-18} = 59\%$, linearity = 70% olefins C_{4-18} ($\text{C}_{8-18} = 50\%$), linearity = 50%	34 35 31
$\text{ZrCl}_4/(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3/\text{Bu}_3\text{P}$ (1:5:2)	benzene, 35 kg/cm 2 , 100 °C	olefins $\text{C}_{12-18} = 10\%$, $\text{C}_{>20} = 26.3\%$	230
$\text{ZrCl}_4/(\text{C}_2\text{H}_5)_2\text{AlCl}/\text{CH}_3\text{SSCH}_3$	chlorobenzene, 35 kg/cm 2 , 100 °C	olefins $\text{C}_{12-20} = 44\%$	231
$\text{ZrCl}_4/(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3/\text{thiophene}$	benzene, 35 kg/cm 2 , 100 °C, 1 h	olefins $\text{C}_{10-18} = 33\%$, $\text{C}_{>20} = 4.8\%$	232
$\text{ZrCl}_4/(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3/\text{BuONa}$ (Al/Zr = 10)	90 °C, 2 h	α -olefins = 80%, linearity = 84%	48, 49
$\text{ZrCl}_4\text{Br}_b/\text{donors}/\text{R}_{3-a}\text{AlX}_a$ (R_2Zn); R = C_{1-20} alkyl; X = Cl, Br, a, b = 0-4; a + b = 4	toluene, 500-5000 psig, 50-300 °C, H_2O , Zr/ H_2O (20:1)	α -olefins, $\bar{M}_n = 108$	234
$\text{ZrCl}_4/(\text{C}_2\text{H}_5)_2\text{Zn}$ (Zn/Zr < 1)	<i>n</i> -heptane, 7 MPa, 130 °C, 30 min	linear α -olefins in $\text{C}_{12-20} = 99.2\%$, $\bar{M}_n = 199$	44

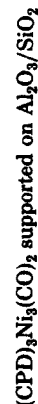
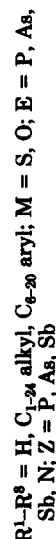
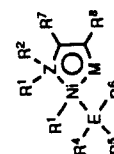
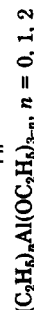
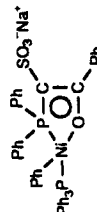
TABLE I (Continued)

catalyst	react condtn	products	yield	ref(s)
ZrCl ₄ /(C ₂ H ₅) ₂ Al (2:1)	120 °C		18 800 g (g of ZrCl ₄) ⁻¹ h ⁻¹ , 4.3% PE	44
ZrCl ₄ /(C ₂ H ₅) ₂ Al (Al/Zr = 4)	120 °C, 7 MPa	linear α-olefins in C ₁₂₋₂₀ = 95.5%	32 000 g (g of ZrCl ₄) ⁻¹ h ⁻¹	43, 44, 208
ZrCl ₄ /(C ₂ H ₅) ₂ AlCl/(C ₂ H ₅) ₂ AlCl ₂ /n-BuOH	chlorobenzene, 890 psig, 70 °C, 30 min	C ₁₂₋₂₀ = 33.2%	1275 g (g of catalyst) ⁻¹ 30 min ⁻¹	43, 29, 235
ZrCl ₄ /R ₃ CCl/(C ₂ H ₅) ₂ Al ₂ Cl ₃ , R = alkyl, aryl	toluene or xylene, 5.6-7 MPa, 120 °C, 15-30 min	olefins C ₂₋₂₀ ≈ 50%, M _n = 254	17 400-39 600 g (g of Zr(OC ₄ H ₉) ₄) ⁻¹ h ⁻¹	226
Zr(OR) ₄ /(C ₂ H ₅) ₂ AlCl/(C ₂ H ₅) ₂ AlCl ₂ (1:1:4), R = C ₃ H ₇ , C ₄ H ₉	heptane, 7 MPa, 130 °C, 30 min	linear α-olefins in C ₁₂₋₂₀ = 99.2%, M _w = 290	10 300 g (g of ZrCl ₄) ⁻¹ h ⁻¹	29, 237
ZrCl ₄ /R ₂ AIR' (4:1), R = alkyl; R' = RO, C ₆ H ₅ O, N(C ₂ H ₅) ₂	n-heptane, 7 MPa, 130 °C, 30 min	linear α-olefin = 99%, M _n = 218-290	1000-13 900 g (g of ZrCl ₄) ⁻¹ h ⁻¹	233, 236
ZrCl ₄ /(C ₂ H ₅) ₂ AlX, X = OC ₂ H ₅ , C ₄ H ₉				50
OC ₁₅ H ₃₁ , OC ₈ H ₁₅ , -O-  -C ₄ H ₉				
Zr(OC ₂ H ₅) ₄ /(C ₂ H ₅) ₂ AlCl ₂ /(C ₂ H ₅) ₂ AlCl (1:1:4)	heptane, 1000 psig, 110 °C, 30 min	linear α-olefins in C ₁₂₋₂₀ = 98.6%, M _n = 242 olefins C ₄₋₄₀		237
(π-C ₃ H ₅) ₂ ZrBr ₂ or (C ₆ H ₅ CH ₂) ₂ ZrBr ₂ /(C ₂ H ₅) ₂ AlCl, (C ₂ H ₅) ₂ AlCl ₂	50-100 °C			238
Zr(acac) ₄ /alkylbenzene/C ₂ H ₅ AlCl ₂ (1:7-50:20-50)	30 MPa, 90 °C, 5 h	70% olefins, bp = 348-500 °C	order of reactivity: toluene > mesitylene > benzene > p-xylene > PPH ₃	239, 229 45
Zr(acac) ₄ /alkylbenzenes/C ₂ H ₅ Al ₂ (C ₂ H ₅) ₂ AlCl ₂ (1:7:30)				
Zr(acac) ₄ /mesitylene/C ₂ H ₅ AlCl ₂ (1:1.6:2.3:9.3)	chlorobenzene	oligomers, flash point = 215 °C, pour point = -20 °C		46
ZrR ₄ , (C ₃ H ₇ O) ₂ ZrCl ₂ , Zr(acac) ₄ /(C ₂ H ₅) ₂ Al ₂ Cl ₃ , R = OC ₂ H ₅ , OC ₁₀ H ₂₁ , (C ₄ H ₉) ₂ N	heptane, 25 atm, 80 °C	α-olefins, C ₄₋₃₀	13 000 mol of C ₂ H ₄ (mol of Zr) ⁻¹ h ⁻¹	36, 240
Zr(OCOR) ₄ or Zr(OSOR) ₄ /(C ₂ H ₅) ₂ AlCl ₃ (1:4), R = alkyl, aryl	5-30 atm, 60-100 °C	olefins C ₄₋₃₀	PE < 0.1%	242
Zr(OCO-i-C ₃ H ₇) ₄ /(C ₂ H ₅) ₂ Al ₂ Cl ₃ (Al/Zr = 17)	toluene, 2 MPa, 80 °C	linear α-olefins = 95-98%, P _n = 506	2500-3856 mol of C ₂ H ₄ (mol of Zr) ⁻¹ , PE = 0.01-0.55%	42
Zr(OCO-i-C ₃ H ₇) ₄ /(C ₂ H ₅) ₂ Al ₂ Cl ₃ (Al/Zr = 17-25)	2 MPa, 80 °C	linear α-olefins = 95-98%, C ₄₋₈ = 45-67%, C ₁₀₋₂₀ = 30-45%	solvent influence on catalytic activity: toluene ≫ n-hep- tane > cyclohexane > gasoline > decene-1; max activity: 17.7 × 10 ⁶ mol of C ₂ H ₄ (mol of Zr) ⁻¹ h ⁻¹	41
Zr(OC ₃ H ₇) ₄ /(C ₂ H ₅) ₂ Al ₂ Cl ₃ (0.55:2.5)	toluene, 20-30 atm, 80-90 °C, 1 h	linear α-olefins = 95%, olefins C ₁₂₋₁₈ = 93-96%, olefins C ₄ = 58%, C ₆ = 29%, C ₈ = 13%	1030 g of C ₂ H ₄ (0.5 g of Zr) ⁻¹ h ⁻¹	83
Zr(O-n-C ₄ H ₉) ₄ /(OC ₂ H ₅) ₂ AlCl ₂ /(C ₂ H ₅) ₂ AlCl/PPH ₃ (8.3:46:1)	toluene, 9 kg/cm ² , 50 °C, 1 h	α-olefins C ₆ = 13%		241
Zr(OCH ₃) ₂ /(C ₂ H ₅) ₂ Al ₂ Cl ₃ ZrCl ₂ Y ₂ /R ₂ AlCl ₃ , α = 1-2; R = C ₂ H ₅ , C ₄ H ₉ ; Y = A ₂ N(=S)S ⁻ , AOC(=S)S ⁻ , (AO) ₂ P(=S)S ⁻ , A = C ₂ H ₅ , C ₃ H ₇ , C ₄ H ₉ , C ₆ H ₅	toluene, 40-80 °C toluene/heptane, 10-35 atm, -10 to 80 °C	α-olefins = 75-85%, C ₁₂₋₂₂ = 19-26%, C ₂₄₋₃₀ = 36-60%; M _c = 56-980	1527 g (g of Zr) ⁻¹ h ⁻¹ , wax, and PE = 10-27%	243 30

$Zr(\text{acac})_2/C_2H_5AlCl_2/(C_2H_5)_2NCS_2Ni/MgCl_2$ (1:25:1:10)	heptane, hexane, 20 atm, 80 °C, 90 min	olefins C_{4-40} , α -olefins = 28-35%, $M_n = 56-560$	2415 g (g of Zr) ⁻¹ h ⁻¹	227
$ZrCl_2X_2/C_2H_5AlCl_2$; X = (CH ₃) ₂ NC(=S)S-, C ₂ H ₅ OC(=S)S-, (C ₆ H ₅ O) ₂ P(=S)S-, (Al/Zr = 18.5-50)	chlorobenzene, 10-40 atm, 80-100 °C	α -olefins, $C_{4-50} = 55-83%$, $M_n = 56-700$	max activity: 6590 g (g of Zr) ⁻¹ h ⁻¹	244
$Zr(\text{acac})_2, Zr(\text{acac})_2Cl$, or $Zr(CH_2C_6H_5)_4$, attached to $(CH_2)_3NCS_2Na$.	tube reactor, 30 atm, -10 to 5 °C	olefins $C_{9-18} = 30-40%$, linearity = 30-78%	max activity: 451 mol of C ₂ H ₄ (mol of Zr) ⁻¹ h ⁻¹	33
$(CH_2)_2C(NH_2)NOH/(C_2H_5)_2Al_2Cl_3$ (Al/Zr = 2-3)				
	silica surface			
MX_nA/R_nAlX_{3-n} ; M = Zr, Hf; X = Cl, Br; A = OR, OOCR; R = alkyl, aryl	100-1000 psig, 0-50 °C	olefins linearity = 90%; $M_{n,av} = 200-400$		215
$MX_n/R_nAlCl/R_nCX$, X = Cl, Br; R = alkyl, aryl; M = Ti, Zr, V, Cr, Mo, W, Fe		olefins $C_{12-22} = 38-50%$		245
NiCl ₂ or Ni(OAc) ₂ /NaBH ₄ /phosphinobenzoic acid (B/Ni = 2; Ni/ligand = 2)	Nickel HO(CH ₂) ₄ OH, 20-70 °C, 500 psig	olefins $C_4 = 8-20%$, $C_{6-10} = 30-50%$, $C_{12-20} = 15-35%$		246
NiCl ₂ ·6H ₂ O/NaBH ₄ /Ph ₂ PCH ₂ COOH	HO(CH ₂) ₄ OH, 500 psig, 25 °C for 15 min, 75 °C for 75 min	olefins $C_4 = 26%$, $C_{6-10} = 31%$, $C_{12-20} = 20%$	2350 g (g of Ni) ⁻¹ h ⁻¹ , 1000 g (g of Ni) ⁻¹ h ⁻¹	247, 248, 262, 264, 265
NiX ₂ /NaBH ₄ /Ph ₂ PCH ₂ CH ₂ COOH/PPPh ₃ , X = Cl, Br	HO(CH ₂) ₄ OH, 40 atm, 100 °C	olefins $C_{4-8} = 41%$, $C_{10-18} = 40.5%$, $C_{20} = 18.5%$		250
NiX ₂ /NaBH ₄ /Ph ₂ PCH ₂ CH ₂ COOH (Ni/B = 1)	glycols, 40 atm, 100 °C	olefins $C_{12-24} = 23%$, $C_{22-42} = 50%$, $C_{>42} = 25%$		251
NiCl ₂ /NaBH ₄ /2Ph ₂ PC ₆ H ₄ COOH	HO(CH ₂) ₄ OH	olefins C_{40}		252
Ni[P(OC ₂ H ₅) ₂ -o-R] ₂ /C ₂ H ₅ /H ₂ SO ₄ (1:25), R = C ₁₋₃ alkyl, alkoxy	chlorobenzene, 0-50 °C			253
Ni(OP(=O)(OR) ₂) ₂ /C ₂ H ₅ Al ₂ Cl ₃ , R = C ₁₋₃ alkyl	benzene, 100 psig, 50 °C	olefins $C_{12-20} = 90%$		254, 255
NiCl ₂ ·6H ₂ O/NaBH ₄ /o-diphenylphosphinophenol	dimethylacetamide, 4.7 bar, 90 °C, 2 h	olefins $C_{8-18} = 67%$, α -olefins = 95-100%, linearity = 100%	conv = 81-95%	256, 257, 259
NiCl ₂ ·6H ₂ O/sodium bis(diphenylphosphino)-4-methylbenzenesulfonate/NaBH ₄ (Ni/B = 1)	C ₂ H ₅ OH, 950 psig, 80 °C	olefins $C_{4-8} = 25.3%$, $C_{10-18} = 8.9%$, α -olefins = 95%		258
L _n Ni/[o-(R)HOC ₆ H ₄ PR ₂], L = COD, R' = CH=C-R'; allyl, RR' = CCR'-CCR, R = alkyl, aryl; R' = alkyl	benzene, 250-1000 psig, 70-80 °C, 2-4 h	olefins $C_{>10} = 70-80%$, linearity = 70-96%	conv = 70-95%	260, 261
Ni(acac) ₂ /haloorganocaluminums/hydrocarbons (Ni/Al = 1:1-100)	hydrocarbons, 32-250 atm, 80-250 °C	$M = 30-300$		263, 266
Ni(acac) ₂ /C ₂ H ₅ Al ₂ Cl ₃ /PPPh ₃ or PBu ₃ (1:3:1-20)	-10 to 0 °C, 3 h	olefins C_{4-8} , $C_{>8} = 13-15%$	conv = 4 × 10 ⁶ mol of C ₂ H ₄ (mol of Ni) ⁻¹ h ⁻¹	94, 266
Ni(CO) ₂ /C ₂ H ₅ Al ₂ Cl ₃ /PPPh ₃	benzene, 400 psig	olefins $C_{>8} = 35.72%$		267
Ni(acac) ₂ /PR ₃ Cl, R = C ₃ H ₇ , C ₄ H ₉ , octyl, decyl	1 atm, 293 K			268
(π -C ₃ H ₅)NiBr/P(i-C ₃ H ₇)(t-C ₄ H ₉) ₂ /C ₂ H ₅ Al ₂ Cl ₃	1 atm, -20 °C	olefins $C_{>8} = 50%$		51, 54
Ni(acac) ₂ supported on (SiO ₂ /Al ₂ O ₃)/C ₂ H ₅ Al ₂ Cl ₃	100 psig, 30-70 °C	olefins $C_{>8} = 34%$		270, 271
Ni(acac) ₂ /(SiO ₂ /Al ₂ O ₃)/C ₂ H ₅ Al ₂ Cl ₃ /PPPh ₃ or PBu ₃	145 °F, 3 h	olefins C_{4-8}	conv = 50%	94
π -C ₂ H ₄ NiCl anchored on γ -Al ₂ O ₃ /C ₂ H ₅ Al ₂ Cl ₃ (1-3% by wt Ni, Ni/Al = 1:2)	1 atm, 20 °C	olefins $C_{6-14} = 16-22%$	178.7 g (g of Ni) ⁻¹ h ⁻¹ , conv 80-85%	272-274
Ni(COD) ₂ /C ₆ H ₁₁ PH ₂ /heptafluorobutyric acid	pentanol, 700 psig		1860 g (g of Ni) ⁻¹ h ⁻¹	275

TABLE I (Continued)

catalyst	react condn	products	yield	ref(s)
Ni(COD) ₂ /P(CH ₃ CO ₂ H) ₂ or PhP(CH ₂ CO ₂ M) ₂ , M = Na, HO(CH ₂) ₂ OH, 50 bar		α-olefins		272, 277
Ni(4-cycloocten-1-yl)bis(trifluoroacetamido)	toluene, 500 psig, 25 °C, 10 h	linearity = 85%	11.5 mol of C ₂ H ₄ (mol of Ni) ⁻¹ 32 g (g of catalyst) ⁻¹ h ⁻¹	278
L ₂ Ni/CF ₃ COCHCOCF ₃ or CF ₃ COOH	benzene, 500 psig, 50–100 °C	olefins C ₄₋₁₀ linearity = 90%	conv = 80% activity of catalyst: SiO ₂ > MgO > ZrO ₂ > Al ₂ O ₃	280, 281
L = COD, τ-allyl, RCH=CHR + Al ₂ O ₃ or not		olefins C ₄₋₁₀ = 5%, PE = 75%; M _w = 95 000		282
Ni(COD) ₂ /CH ₃ P(CH ₂ COOH) ₂	benzene, 500 psig, 50–100 °C	olefins C ₄₋₁₀ = 97%		249
Ni(COD) ₂ /RP(OR)CH ₂ COCH ₃ , R = alkyl		linearity = 90%		249
Ni(COD) ₂ /P(X)OR(R) supported on SiO ₂ , MgO, ZrO ₂ , Al ₂ O ₃ ; X = carboxymethyl; R = alkyl	aromatic solvents	linear α-olefins = 99.6%	6000 mol of C ₂ H ₄ (mol of Ni) ⁻¹	284, 285
Ni(COD) ₂ or Ni(τ-allyl) ₂ /9-(carboxymethyl)-9-phosphabicyclo[3.3.1]nonane	benzene, 500 psig, 100 °C	linear α-olefins = 91–95%, C ₄₋₆ = 37%, C ₈₋₁₂ = 34%, C ₁₂₋₂₀ = 29%	conv = 53%; 2.4 g (g of Ni) ⁻¹ h ⁻¹	286
Ni(COD) ₂ /RP(OR)CH ₂ X, X = hydroxymethyl, mercaptomethyl, hydroxycarbonyl, hydroxycarboxymethyl; R = alkyl	n-heptane, 500–700 psig, 50 °C, 15 h	α-olefins = 96%, linearity = 98%, C ₄₋₆ = 34.3%, C ₁₀₋₁₈ = 41.7%, C _{>20} = 24%	conv = 68%; 6.5 g (g of Ni) ⁻¹ h ⁻¹	287, 279
Ni(COD) ₂ /RPCH ₂ C(=O)NAs, R = alkyl, phosphine group; A = hydrogen, aromatic group, e.g., Ph ₂ PCH ₂ C(=O)NPh ₂	benzene, 500 psig, 25–100 °C	olefins C ₄₋₂₀ = 50%, C _{>20} = 50%; linearity = 92%		288
Ni(COD) ₂ /Ph ₂ P=CHC(=O)X, X = OH, OC ₂ H ₅ , NPh ₂	toluene, 50 bar, 50 °C	α-olefins = 98%, linearity = 99%, C ₄₋₂₄ = 98–99%	6000 mol of C ₂ H ₄ (mol of Ni) ⁻¹	55, 291, 292, 294
Ph(PPh ₂) ₂ Ni(Ph ₂ PCHC(Ph)O) or Ni(COD) ₂ /Ph ₂ PCH ₂ COOH	benzene, 10–80 bar, 75 °C	α-olefins = 99%, C ₄₋₂₂	conv = 93%	290, 293
Ni(COD) ₂ /Ph ₂ PCH ₂ COOH	(SS)-flow reactor, 68 bar, 50 °C	α-olefins = 7–64%, linearity = 26–92%, C ₈₋₁₆		60
Ph(PPh ₂) ₂ Ni(Ph ₂ PCHC(Ph)O) or (COD)Ni(Ph ₂ PCH ₂ COO) supported on Al ₂ O ₃ /SiO ₂ (SS) or binding over the phosphine or P=O chelate ligands to polystyrene (PS)	(PS)/toluene, 40 bar, 75 °C	α-olefins = 96–99%, linearity = 99%, C ₈₋₁₆		60, 307
Ni(COD) ₂ /Ph ₂ P/L, L = Ph ₂ As=CHCOPh, Ph ₂ As=C(COPh) ₂ , Ph ₂ AsCH ₂ COOH	toluene, 15 bar, 40 °C	α-olefins = 70%, linearity = 95%	1600 mol of C ₂ H ₄ (mol of Ni) ⁻¹ h ⁻¹	56
(COD)Ni[CH(C(R)O)] ₂ , R = CH ₃ , CF ₃	toluene, 75 °C, 5 MPa	α-olefins = 17–24%, linearity = 67–82%, C ₄₋₂₄		53, 55
[Ph ₂ PCH ₂ (CF ₃) ₂ O]NiH(PCy ₃)	toluene, 50 bar, 50 °C	(C ₁₀₋₂₄ = 21%) α-olefins = 98%, linearity = 99%, C ₄₋₃₀	5000 mol of C ₂ H ₄ (mol of Ni) ⁻¹ h ⁻¹	201
(C ₂ H ₅) _n Al(OC ₂ H ₅) _{3-n} , n = 0, 1, 2	aromatic solvents, polar solvents, 14.6 atm, 50 °C, 120–180 min	α-olefins = 91%	without Al complex 2 × 10 ⁴ g (g of complex) ⁻¹ ; for Al/Ni = 200–5.2 × 10 ⁶ g (g of complex) ⁻¹	57, 58, 289, 295–297, 378
	80 °C, 500–1000 psig, 80 °C	linear α-olefins		295, 377
	CH ₃ OH/H ₂ O (0.5–20% H ₂ O), 20–100 °C, 10–300 psig	olefins C ₆₋₈ = 48%, C ₁₀₋₁₈ = 52%	selectivity = 90%	445
R ¹ –R ⁸ = H, C ₁₋₂₄ alkyl, C ₆₋₂₀ aryl; M = S, O; E = P, As, Sb, N; Z = P, As, Sb	benzene, 450 psig, 150 °C, 1 h	olefins C ₄₋₁₄ , C ₈₋₁₄ = 29.5%	10 ⁵ mol of C ₂ H ₄ (mol of catalyst) ⁻¹ h ⁻¹	296–299
(CPD) ₂ Ni ₃ (CO) ₂ supported on Al ₂ O ₃ /SiO ₂				



(CPD)Ni(π -C ₆ H ₇) supported on Al ₂ O ₃ /SiO ₂	heptane, 14–21 atm, 50–60 °C, 1 h	olefins C _{9–10} = 16%, C _{12–22} = 10%	conv = 84%	300, 301
(CPD)Ni(π -C ₆ H ₇) supported on Al ₂ O ₃ /SiO ₂ /CH ₃ SSCH ₃ or SNi(octanoate) ₂ /(C ₂ H ₅) ₃ Al	800–1000 psig, 90 °C	olefins C _{10–22} – 17% internal olefins C _{14–30} which are isomerized and metathesized and recycled		302 205
(C ₂ H ₅) ₃ Al	Aluminum	oligomers	temperature effect on product distribution	304
(C ₂ H ₅) ₃ Al/ <i>i</i> -Bu ₃ Al	200–2000 psig, 100–150 °C	α -olefins C _{4–10} C _{8–10} = 19.3%	2–6 mol of C ₂ H ₄ (mol of Al) ⁻¹	305
(C ₂ H ₅) ₃ Al/Bu ₃ Al 5% in solvent	<i>n</i> -tetradecane, 500–700 psig, 120 °C	olefins C _{10–40} (1) reactor growth, (2) reactor ethylene displacement		306, 317
R ₃ Al(<i>i</i> -Bu ₃ Al) ₂ O, R = alkyl C _{6–8} (C ₂ H ₅) ₃ Al	500–1250 bar, 160–230 °C kerosene, 248 °F, 1500 psig, 15 min	α -olefins C _{10–40} α -olefins = 62%		65 308
(C ₂ H ₅) ₃ Al (0.6 mol/L)	20–60 kg/cm ² , 180 °C, 3–7 h	olefins C _{10–20} = 70–77%, linearity = 75%	conv of C ₂ H ₄ = 40–140 L/h	310, 313
(C ₂ H ₅) ₃ Al	60 kg/cm ² , 180 °C, 7 h	olefins C _{6–20} (Ethyl Corp. Process)		78, 311
(C ₂ H ₅) ₃ Al	<i>n</i> -heptane, diisobutane, 395–1000 atm	linear α -olefins C _{4–40} max C _{12–16} (Gulf Research Process)	conv = 53–55%	79, 312
(C ₂ H ₅) ₃ Al/Ph ₂ NH, R ₂ S (0.25–500 parts/(10 ⁶ parts of (C ₂ H ₅) ₃ Al), R = alkyl C _{6–16}) (C ₂ H ₅) ₃ Al/Ni, Co, Pt (C ₂ H ₅) ₃ Al/polyethers	4–40 atm, 285–615 °F 100 °C 50 atm, 150 °C	olefins C _{4–40}	amine prevents PE formation	66, 67, 314 315–318 319
(C ₂ H ₅) ₃ Al/polyvinylalcohol or phenolic resins Al _{1.5} max/CCl ₄ (1:0.05–1)	40 atm, 100 °C, 150 min hydrocarbons, 40 atm, 130 °C	α -olefins C _{2–24} linear α -olefins = 65% in C _{6–18} oligomers α -olefins C _{6–40} C _{4–18} = 75% oligomers M_w = 100 (35%), M_w = 380 (17%)	6.6 g (g of Al) ⁻¹	68 320, 321
(π -allyl)Ru(CO) ₂ X, X = Cl, Br	Ruthenium	olefins C _{4–14} C _{4–8} = 63%, C _{6–14} = 34%		62
[Pd(CH ₃ CN) ₄](BF ₄)/CH ₃ CN	Palladium	olefins C _{4–10}		322
Hg(OAc) ₂ /(C ₂ H ₅) ₂ NH/HOCH ₂ CH ₂ NH ₂	Mercury	olefins C _{6–8}		63
BF ₃ /Al ₂ O ₃ (BF ₃ 1–20% by wt) hydrogen mordenite	Heterogeneous Inorganic Systems 100 psig, 150 °C 500 K	olefins, aromatic hydrocarbons, polyphenylene olefins C _{10–20} = 41.1% olefins C _{12–14} (max C ₁₄) olefins C _{>10} = 26% oligomers olefins C _{6–14} = 85% olefins, paraffins, aromatic hydrocarbons	conv = 51.4%	192 329
Ni/(Al ₂ O ₃ /SiO ₂) (0.72% by wt Ni) MoO ₃ /Al ₂ O ₃ Ni/NaY zeolite NiO/Al ₂ O ₃ /SiO ₂ , NiO/Al ₂ O ₃ (H ₂) K/graphite, K/KCl, K/Na ₂ O H/ZSM-5, HNA Y	3500 kPa, 115 °C, 2 h 3500 kPa, 100–150 °C 500 lb/sq, 200–300 °C 300–373 K	olefins C _{>30} = 65–75%, aromatic hydrocarbons = 20%	conv = 99.3%	323 324 325 75, 76 326 137, 327, 328
H/ZSM-5 zeolite OGO-1 zeolite	flow reactor, 300–390 °C flow reactor, 0.1 MPa, 390–400 °C, 200 h		conv = 15%	71–74, 141 408

The system $\text{Zr}(i\text{-PrCOO})_4/\text{Et}_n\text{AlCl}_{3-n}$ ($n = 1.5-2$) served as a model for the study of the influence of reaction conditions on the ethylene oligomerization reactions.³⁹⁻⁴² The maximum oligomerization rate was observed for the system with $n = 1.7$. A change of n from 1.5 to 1.7 results in an increase of branched olefins (with internal C=C bonds) content in the products. The main reason for this phenomena is the relatively higher concentration of forming α -olefins in comparison with that of ethylene in the reaction medium caused by the very high activity of the catalysts. This enhances the catalyst reaction with higher α -olefins.⁴² Increasing n from 9.5 to 17.3 decreased the yield and the molecular weight of the oligomers.⁴¹

An increase of the alkyl (R) chain length in the $\text{Zr}(\text{RCOO})_4$ salts decreases the catalyst activity.⁴² Raising the reaction temperature from 333 K to 373 K results in increase of the reaction rate, the reaction yield and the average molecular weight of the α -olefins. A higher reaction temperature (393 K) did not increase the reaction yield, but increased the α -olefin chains.⁴¹

When the ethylene pressure is raised during the ethylene oligomerization, a higher reaction rate and selectivity with unchanged oligomer molecular weight is achieved.

Catalyst activity and selectivity of $\text{Zr}(\text{RCOO})_4/\text{Et}_n\text{AlCl}_{3-n}$ system is altered when the solvent is changed and increases in the order toluene > n -heptane > cyclohexane > ligroin. This is related to the lower ethylene solubility in these solvents, resulting in competitive, higher α -olefins cooligomerization. The same relationships are observed for other zirconium catalysts. For the $\text{ZrCl}_4/\text{Et}_2\text{AlCl}$ system increasing of Al/Zr ratio from 0.25 to 4.0 gave better yields (6000 to 32000 g of oligomer $(\text{g of Zr})^{-1} \text{h}^{-1}$), lower average molecular weights, (224 to 150) and higher α -olefin selectivity (95.5–99.9%), respectively.⁴³ When Et_2AlCl is changed to Et_2Zn in this system, lower yields are obtained (6300 g oligomer $(\text{g of Zr})^{-1} \text{h}^{-1}$) with a higher α -olefin selectivity (99.1–99.8%) and higher oligomer molecular weight (229–285).⁴⁴

Catalysts, giving C_{6-20} olefins in very high yield and purity (95%), containing Zr halides, organoaluminum compounds and sulfides, disulfides, thiophenes, thio-urea, phosphines or primary amines, are described in Idemitsu Petrochemical Co. Ltd. patents.²³⁰⁻²³²

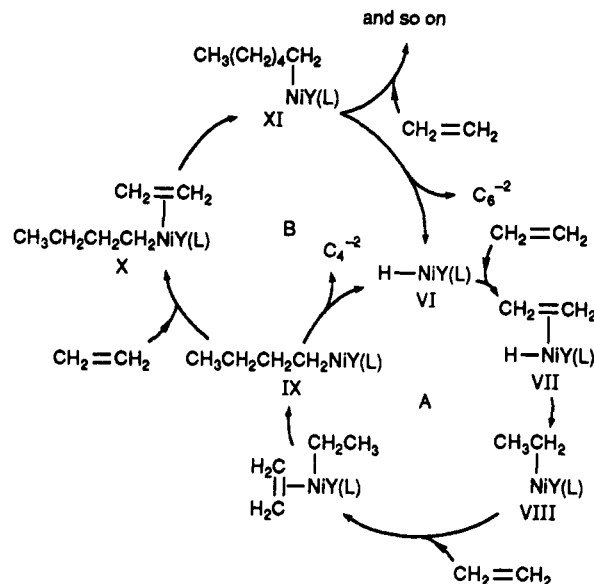
The $\text{ZrCl}_4/\text{EtAlCl}_2$ system is not active in the ethylene oligomerization and the catalysts $\text{ZrCl}_4/\text{BuLi}$ and $\text{ZrCl}_4/\text{Bu}_2\text{Mg}$ exhibit very small activity in this reaction.⁴⁴ When Et_3Al is used as modifier for ZrCl_4 , a very active but relatively less selective (4.8% of polyethylene in the products) oligomerization catalyst is obtained.

Similar catalytic behavior is observed in the case of the $\text{Zr}(\text{acac})_4/\text{EtAlCl}_2$ ⁴⁵⁻⁴⁶ and $(\text{C}_3\text{H}_7)_4\text{Zr}/\text{Et}_3\text{Al}_2\text{Cl}_3$ ³⁶ catalysts.

The He and co-workers^{48,49} EPR investigations of the systems $\text{ZrCl}_4/\text{Et}_2\text{AlCl}$ and $\text{ZrCl}_4/\text{Et}_3\text{Al}_2\text{Cl}_3/\text{BuONa}$ have indicated that it is possible to combine the catalysts deactivation with the reduction reaction namely, Zr(IV) to Zr(III).

In the system $\text{ZrCl}_4/\text{Et}_2\text{AlX}$ ⁵⁰ where X = OEt, $\text{O-C}_{15}\text{H}_{31}$, OC_6H_5 , (2,6-di-*tert*-butylphenyl)oxy, $\text{N}(\text{Et})_2$, and 2,2,6,6-tetramethylpiperidine, the catalyst activity in ethylene oligomerization depends strongly on the ligands around aluminum. The bulky ligands decrease

SCHEME VI. Catalytic Cycle of Ethylene Oligomerization in the Presence of a Nickel Catalyst^{1,50}



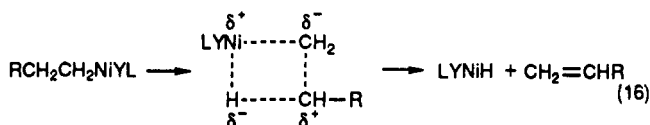
catalyst activity. The best yield was obtained for X = NEt_2 ($M_n = 285$). All the catalyst systems with Et_2AlX as modifier were more active than those Et_2AlCl . Thus a replacement of chlorine acceptor ligand in Et_2AlCl with a donor ligand X results in higher oligomerization yields. Whereas with the $\text{TiCl}_4/\text{Et}_2\text{AlX}$ systems, the presence of acceptor X ligands resulted in a more active catalyst.

In conclusion, it can be stated that zirconium catalysts are generally more active than titanium ones. The catalyst activity for ethylene oligomerization in presence of zirconium catalysts is in the range, 15–30 kg $(\text{g of Zr})^{-1} \text{h}^{-1}$.^{41,44,50} Selectivity to linear α -olefins approaches 99%. A constant ethylene supply is necessary to avoid the formation of branched olefins with internal C=C bonds. Such olefins are the products of the higher olefins cooligomerization and isomerization when the ethylene concentration is too low in the reaction medium.

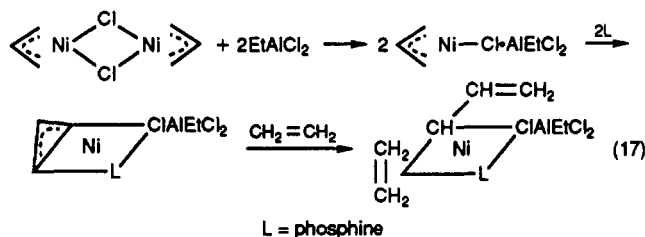
III.1.3. Nickel

Nickel complexes are the most common group of the olefin oligomerization catalysts exhibiting the highest activity and selectivity to linear α -olefins. The oligomers follow a Schulz-Flory type distribution. The nickel catalyst complexes can be divided into two groups: nickel(II) compounds modified with alkyl or hydride main-group metal derivatives (Ziegler-Natta type catalysts) and chelated nickel compounds with a Ni-C bond.

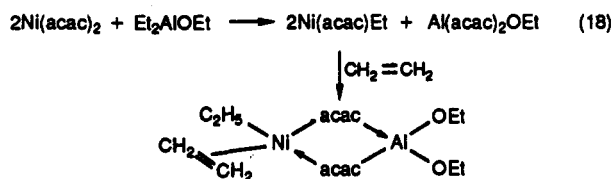
The ethylene oligomerization catalyst cycle in presence of nickel catalyst, HNiYL where, Y = acyl, carboxyl, halogen; L = phosphine, is shown on Scheme VI. Ethylene coordination to the complex VI with the Ni-H bond, which is the catalyst's active center, gives the complex VII. The coordinated ethylene insertion into the Ni-H bond with formation of Ni-C₂H₅ group (complex VIII) begins the catalytic cycle via complexes IX, X, and XI. The chain transfer occurs through the β -hydrogen elimination from the oligomer chain in the complex XI by the nickel atom whereby the Ni-H bond is restored and oligomer liberated e.g.



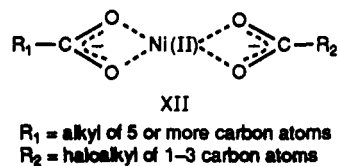
Formation of the Ni-H or Ni-alkyl bonds in nickel compounds is responsible for their catalytic activity in olefin oligomerization. This process for the system: $(\pi\text{-C}_3\text{H}_5)\text{NiCl}/\text{Et}_n\text{AlCl}_{3-n}$ ($n = 1, 2$) is proposed as follows:¹



In the system: $\text{Ni}(\text{acac})_2/\text{Et}_2\text{AlOEt}$ (1:1) nickel alkylation occurs according to reaction 18:⁵¹



Muzzio and Löffler⁵² have proposed the following mechanism of the Ni-H bond formation for the catalyst XII:

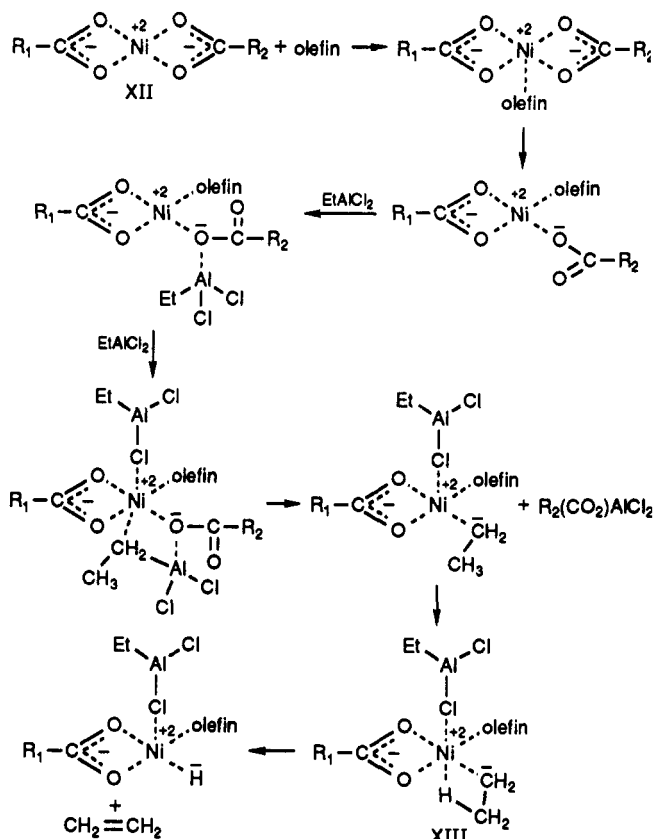


EtAlCl_2 and Et_2AlCl as a mixture are the necessary cocatalysts in this system. The mechanism of its action is presented on Scheme VII.

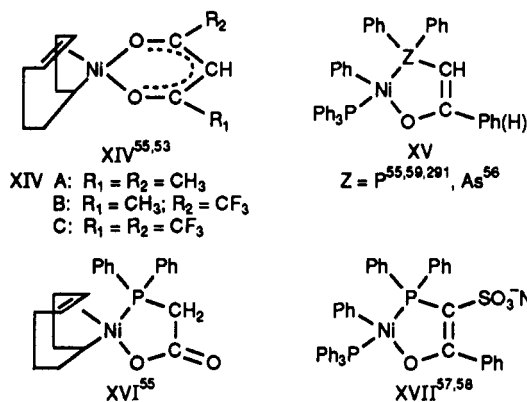
The reaction was carried out by adding at the beginning the nickel salt XII to the olefin. Next the organometallic compound was added. If the nickel salt were mixed with the organometallic compounds with no olefin present, the nickel salt would be reduced and would lose its catalytic activity. The first step of the reaction consists of the olefin coordination to the nickel atom. This helps to avoid reduction of the nickel in the complex XII with added organoaluminum compound. At first EtAlCl_2 complexes with one of the oxygen atoms in the complex XII. Additional aluminum compound is coordinated to the nickel through the chlorine bridge; and thus, is able to neutralize negative charge on the oxygen atom which in turn helps the salt $\text{R}_2\text{COOAlCl}_2$ to split off. Thus the nickel in the complex XIII is coordinatively unsaturated. Internal rearrangement leads to formation of Ni-H bond.

Many chelated nickel complexes are highly active and

SCHEME VII. Mechanism for Hydride Formation in a Nickel-Catalyzed Olefin Oligomerization⁵³



selective in the ethylene oligomerization without added organoaluminum compound e.g.

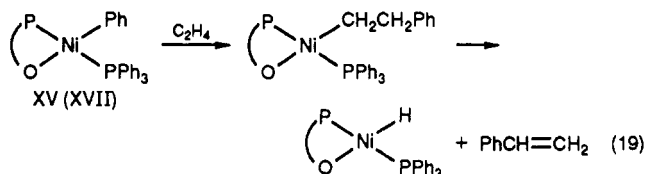


Complexes of type XIV are very active catalysts for the oligomerization of ethylene. Linearity of 80% can be obtained in the C_3 oligomers⁵³ (XIV C). Complex XV has been found as the most interesting ethylene oligomerization catalyst. It converts ethylene at 50 °C and 10–100 bar to α -olefins possessing 99% linearity and >95% α -olefin content.²⁹¹ The geometric distribution of olefins can be modified by pressure and addition of Ph_3P . Increasing the $\text{Ph}_3\text{P}/\text{Ni}$ ratio decreases the catalyst activity. Substitution Ph_3P in complex XV by trialkyl phosphine inactivates the system. When (α -naphthol)₃P substitutes Ph_3P , 70% of linear PE is obtained in the products of ethylene oligomerization.²⁹⁴

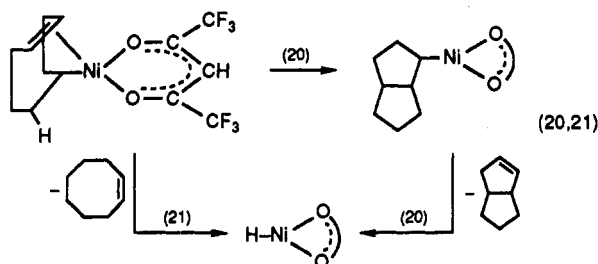
Complexes similar to XV may be formed on reacting bis 1,5-cyclooctadiene nickel(O) with $\text{Ph}_2\text{PCH}_2\text{CO}_2\text{H}$,⁴⁴⁶ thiolactic acid,⁴⁴⁷ *o*-mercaptobenzoic acid,⁴⁴⁸ phospho-

rous ylides,⁴⁴⁹ or $\text{Ph}_2\text{PCH}_2\text{C}(\text{CF}_3)_2\text{OH}$.²⁰¹ All these systems have been patented by Shell and are effective in the Shell higher olefin process.⁹⁰

The XV and XVII derivatives do not have Ni-H bonds. These bonds are formed during oligomerization reaction probably through ethylene insertion into the Ni-Ph bond and the immediate split off of a styrene molecule^{58,59} (eq 19):

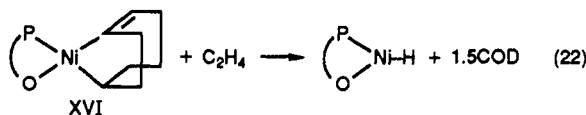


In the chelated complexes XIV the Ni-H bond is formed as a result of reactions 20 and 21.⁵³

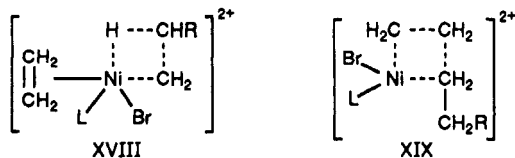


As stated earlier, reaction 20 is more favored than reaction 21. During ethylene oligomerization in presence of the complex XIV mainly bicyclo(3.0.0)octene-2 (beside a small amount of 1,5-cyclooctadiene) was found.⁵³

The Ni-H bond in the reaction of ethylene with the complex XVI is formed as follows:⁵⁹



Active nickel complexes in the ethylene oligomerization have generally a square-planar structure. Their activity and selectivity depend on the nature of ligands surrounding the nickel ion. The more basic the phosphine (L) ligands and greater their bulk in the complex, ($\pi\text{-C}_3\text{H}_5$)NiBrL/Et₃Al₂Cl₃, the higher the oligomer molecular weight is.^{51,54} This phenomena is explained by the β -hydrogen elimination from the five or more coordinated intermediate XVIII, whereas the olefin insertion into the nickel-alkyl bond occurs through the less-hindered intermediate XIX:



An increase in steric volume of the phosphine L helps in the formation of the structure XIX and the growth of the oligomer chain. A similar effect of an increase in the oligomer molecular weight is observed when there is a decrease in the electron density in the nickel ion in the complex XIV. An exchange, in this complex, of donor alkyl ligands for CF₃, which causes the withdrawal of electron from the nickel ion, diminishes the insertion reaction barrier and therefore the growth of the oligomer chain and its linearity.⁵⁵

TABLE II. Modification of XVII by Aluminium Alkoxides⁵⁷

aluminium alkoxide	blank run	AlEt ₂ -OEt	AlEt(OEt) ₂	Al(OEt) ₃
Ni ylide (XVII), g	0.0025	0.0025	0.0025	0.0025
Al/Ni, mol	0	200	200	200
temp, °C	50	50	50	50
reaction pressure, atm	14.6	14.6	14.6	14.6
reaction time, min	120	180	180	185
yield of oligomers g (g of XVII) ⁻¹	700	18000	16700	14800
yield of oligomers mol (mol of XVII) ⁻¹	2 × 10 ⁴	5.2 × 10 ⁵	4.8 × 10 ⁵	4.2 × 10 ⁵
1-alkene, content, %		90.3	90.7	90.2

In the complexes XV and XVI, donor character of the O-P ligand weakens the Ni-H and Ni-C bonds. However, this effect does not influence the β -H-elimination reaction. In summary, these complexes oligomerize ethylene to long-chain α -olefins without C=C bond isomerization; so, the obtained selectivity for linear α -olefins is very high 99–100%.⁵⁵

A very high selectivity of ethylene oligomerization is also obtained when [(Ph₂PCH₂C(CF₃)₂O)NiH(PCy₃)] is used as a catalyst, i.e. 99% of linear and 98% α -olefins C₄₋₃₀ are products of this reaction.²⁰¹ This high selectivity of the nickel complex is connected with the steric effects of the bulky phosphines rather than with their electronic properties.⁵⁵

The ylide nickel complexes XV, XVI, and XVII are known to be the most active and selective catalysts of the olefin oligomerization. The recently described modification of the complex XVII with alkoxyalkyl-aluminum compounds gave one order of magnitude higher active systems (Table II).⁵⁷ In this case, the main products are linear α -olefins C₄₋₄₀. Some internal C=C bond olefins are also obtained.^{58,59} Other ethylene dimers and trimers were obtained when other organo-aluminum compounds (Et₂AlCl, *i*-Bu₂AlCl, or EtAlCl₂) were used as cocatalysts. The system XVII modified with Et₂AlOEt loses with time its catalytic activity and faster at higher temperatures.⁵⁷

Using strong polar solvents as glycols^{246-248,265} pentanol,²⁷⁵ methanol,³⁷⁸ and methanol/H₂O (0.5–20% H₂O)⁴⁴⁵ for the catalytic system similar to XV and XVII allows the catalyst solution to separate in better grade from oligomer phase.

The complexes Ph(Ph₃P)NiOCHPhCHPPh₂ (XV), and ($\eta^3\text{-C}_8\text{H}_{13}$)NiOOCCH₂PPh₂ (XVI) were heterogenized on alumina-silica and polystyrene supports. The systems supported on alumina-silica gels were less active than their homogeneous analogues. However, complex XV, bonded to the polystyrene chain through phosphine or P=O ligands, forms active and highly selective (99%) catalysts, giving high molecular linear α -olefins.⁶⁰

III.1.4. Other Metals

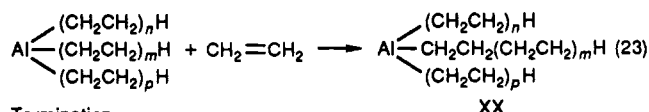
($\pi\text{-CH}_2\text{=CHCH}_2$)Ru(CO)₃X (X = Br, Cl) oligomerize ethylene to C₁₄ linear and branched olefins.⁶² The mercury complex Hg(OOCCH₃)₂ + HOCH₂CH₂NH₂ + (C₂H₅)₂NH is only a slightly active in this reaction.⁶³

III.2. Aluminum

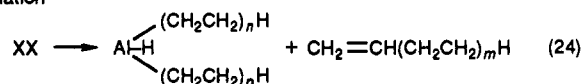
Ethylene oligomerization in the presence of alkyl-

aluminum compounds occurs according to the following reactions:⁶⁴

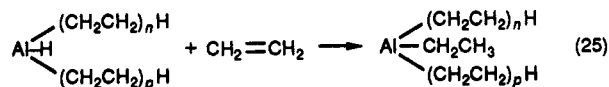
Propagation



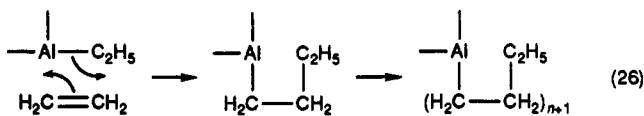
Termination



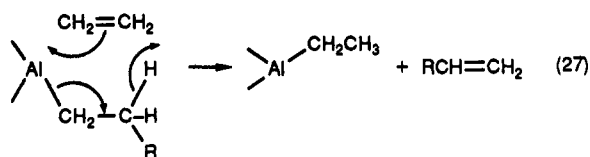
Thermal decomposition of the aluminum-alkyl bond yields the Al-H bond and α -olefin. At the end of the process the hydridoaluminum compound reacts very fast with ethylene, as follows:



The Al-CH₂CH₃ bond can initiate the oligomer chain growth by inserting the next ethylene molecule, and thus beginning a cycle of ethylene oligomers production. The chain growth occurs through a four-center intermediate:⁶⁵



The chain-termination reaction involves a six-center transition state:



Thermal decomposition (reaction 24) of the Al-R bond is considerably slower than the ethylene insertion into the Al-H bond (reaction 25). Thus, at lower temperatures, the oligomer growth reaction gives mainly high molecular weight products. At higher temperatures, 463 K, thermal decomposition of the Al-R bond begins to dominate the C₁₂ olefins becomes the main products.⁶⁹ The product composition as a function of the reaction temperature is shown on Figure 2.⁶⁴

An increase in the reaction pressure increases the ethylene conversion and the amount of linear long-chain oligomers.⁶⁵ To avoid polyethylene formation, sulfur (R-S-R)⁶⁶ or nitrogen compounds are added to the reaction mixture.

Triethylaluminum was heterogenized by binding to polymers possessing hydroxy groups such as polyvinyl alcohols⁶⁸ or phenol resins.^{68,69} The ethylene oligomers obtained in their presence are C₈₋₁₈ olefins with 75% content of α -isomers.

III.3. Inorganic Heterogeneous Catalysts of Ethylene Oligomerization

Various zeolites, e.g. H-ZSM-5, have been investigated as ethylene oligomerization catalysts.⁷⁰⁻⁷³ They possess some of the positive heterogeneous catalyst properties like the possibility of carrying out reactions in a flow system, easy catalyst regeneration, and product separation

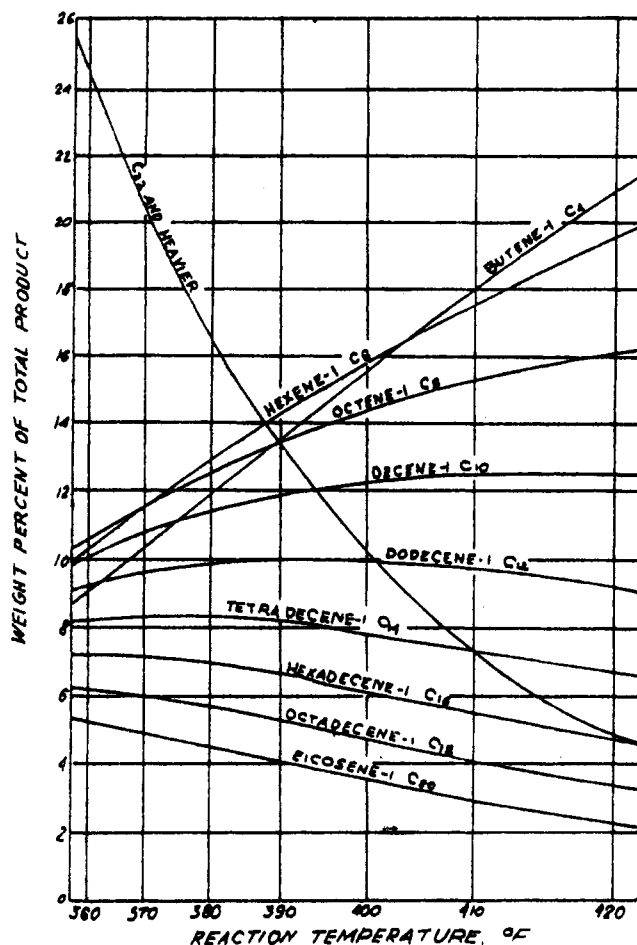


Figure 2. Effect of temperature on product distribution in ethylene oligomerization in the presence of (C₂H₅)₃Al, the Gulf Process.⁶⁴

ration but they have shown poor selectivity to α -linear olefins; a large amount of branched and cyclized olefins, paraffins, and aromatics is in the products especially when ethylene oligomerization is carried out at higher temperatures, 570 K.^{70,71} Hydrocarbon cracking is also observed at these temperatures. Only in presence of high silica zeolites possessing strong Brønsted acid sites are linear oligomers obtained. In this case, mechanism of the ethylene oligomerization assumes cationic character.⁷⁴

Transition-metal oxides and salts, supported on inorganic gels such as alumina and alumina-silica, oligomerize ethylene to α -olefins C₆₋₁₀. On the surfaces of these catalysts Brønsted acid and coordinative centers exist, which together are responsible for the olefin oligomerization. EPR investigations suggest that Ni(I) ions are the ethylene oligomerization centers in the NiO-Al₂O₃ and NiO-Al₂O₃-SiO₂ systems.^{75,76}

III.4. Industrial Ethylene Oligomerization Processes

Large industrial scale production of α -olefins is carried out by Gulf Oil Chemical Co.,^{64,79} Ethyl Corp.⁷⁷ and by Shell Oil Co.^{59,77,80,81,82} The Gulf and Ethyl processes use Et₃Al as a catalyst although they differ in some details. In the Ethyl process unlike in the Gulf process the products are recycled in order to increase the amount of the most desirable linear α -olefins C₆₋₁₄. It

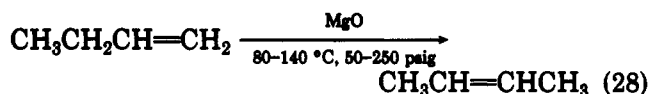
TABLE III. Analyses of α -Olefins from Ziegler-type Oligomerization of Ethylene with Recycle (Data from Ethyl Corp.)⁷⁷

	wt %						
	C ₆	C ₈	C ₁₀	C ₁₂	C ₁₂₋₁₄	C ₁₄₋₁₆	C ₁₆₋₁₈
linear α -olefins	97.5	96.5	96.2	93.5	87.0	76.9	62.7
linear olefins with internal double bonds	0.6	1.2	1.6	1.5	4.2	5.6	8.2
β -branched α -olefins	1.9	2.3	2.2	5.0	8.8	29.0	29.1
paraffins	0.1	0.6	0.3	0.4	0.4	0.4	0.8

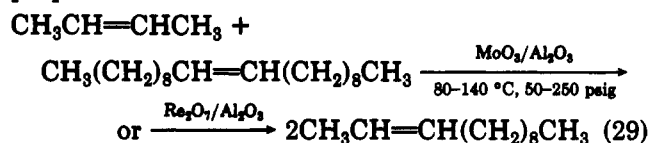
leads, unfortunately, to higher branched olefins content in the products as a result of higher α -olefins reaction with alkylaluminum compounds.⁷⁷

The Ethyl⁷⁸ process is carried out at 393 K under 210 psig pressure and the Gulf process at 463 K under 4000 psig uses 14% Et₃Al in heptane solution as catalyst. The ethylene conversions reach 85%. The product composition of these two processes is given in Tables III and IV.⁷⁷

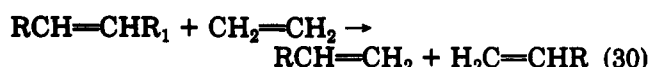
The most modern ethylene oligomerization process—SHOP (Shell Higher Olefins Process) consists of three steps: ethylene oligomerization, oligomers isomerization, and comethathesis.^{59,80,82,294} (This process scheme is presented on Figure 3. Ethylene oligomerization is a catalytic process, with a homogeneous catalyst consisting of nickel chloride and the potassium salt of *o*-(diphenylphosphino)benzoic acid in 1,4-butanediol. The oligomerization reactors are operated at 80–120 °C and 1000–2000 psig. The ratio of reaction is controlled by the rate of catalyst addition. High partial pressure of ethylene is required for good rate of reaction and high linearity of the α -olefins product. Catalyst for oligomerization is dissolved in a solvent that is largely immiscible with the α -olefin product. After the reaction, a product is separated from catalyst solution and excess ethylene gas. Catalyst and ethylene are recycled. The oligomerization reaction provides a range of α -olefins with an even numbers of carbon atoms from C₄ to C₄₀. These are fed into a distillation column and split into three fractions, a C₄₋₈ fraction, the desired C₁₀₋₁₄ fraction, and a heavy C₁₆₋₄₀ fraction. The light and heavy fractions are fed to an isomerization reactor where α -olefins are isomerized to internal olefins:



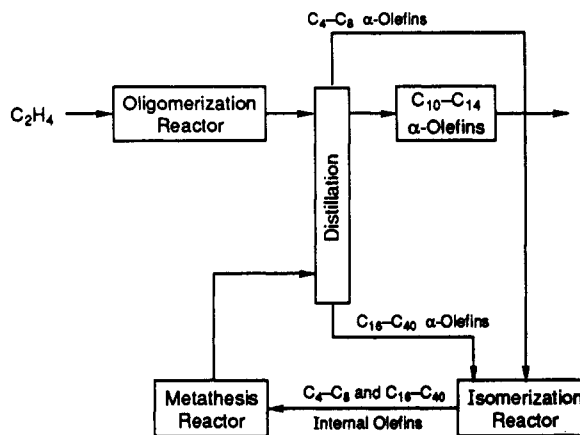
The internal olefins pass to the metathesis reactor where the short- and long-chain internal olefins disproportionate:⁸²



When higher internal olefins are reacted with ethylene α -olefins are obtained:²⁹⁴

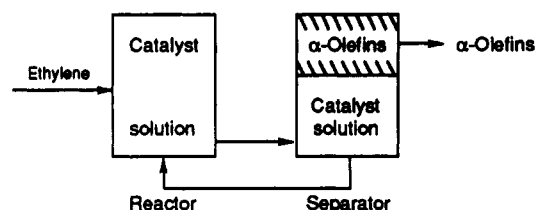


The C₁₀₋₁₄ olefin fraction is fed into a hydroformylation reactor where it is converted to the corresponding straight-chain aldehydes and then to alcohols. When



1. Oligomerization
2. Isomerization
3. Metathesis

a. Shell higher olefin process (SHOP)



b.

Figure 3. Shell higher olefin process (SHOP)^{59,82}. Part a shows the Shell higher olefin process. Part b shows catalyst recycling making the most of two-phase solvent system.

TABLE IV. Composition of α -Olefin Mixture from Catalytic High-Temperature Ethylene Oligomerization (wt %) (According to Data from Gulf Oil Chemical Co.)⁷⁷

	wt %						
	C ₆	C ₈	C ₁₀	C ₁₂	C ₁₄	C ₁₆	C ₁₈
linear α -olefins	97.0	96.0	95.0	94.0	93.0	92.0	91.0
β -branched α -olefins ^a	1.4	2.5	3.4	4.6	5.6	6.6	7.8
paraffins	1.4	1.4	1.4	1.4	1.4	1.4	1.4

^a Including very small amounts of olefins with internal double bonds.

the cobalt carbonyl complex catalyst is used causing the internal C=C bond migration to α -position in the olefins, the C₁₀₋₁₄ internal olefins are passed to the hydroformylation reactor.

α -Olefin oligomerization products are characterized by a geometric molar growth factor defined as $K = (\text{moles of } C_{n+2} \text{ olefin}) / (\text{moles of } C_n \text{ olefin})$ (31)

Weight distribution of various α -olefin oligomerization product fractions is function of K .⁸⁰ Control of K factor is the key to the process, since it not only sets the product distribution in α -olefin oligomerization, but also determines the average carbon of the entire SHOP product. K factor can be readily varied by adjusting the catalyst composition. The SHOP process gives highly pure linear α -olefins of the range C₆₋₁₈ as is shown in Table V.⁷⁷

For comparison, the products composition of the Gulf Corp., the Ethyl Corp. and the SHOP processes are presented in Table VI.⁷⁷

A new ethylene oligomerization process, using as a catalyst the nickel salt of organic acids/Et₃Al system,²⁰⁵ has been recently patented in the United States. Also, in the USSR, the systems Zr(OPr)₄/Et₃Al₂Cl₃ and

TABLE V. Typical Quality of α -Olefins from SHOP Process⁷⁷

hydrocarbon type	composition, wt %						
	C ₆	C ₈	C ₁₀	C ₁₂	C ₁₄	C ₁₆	C ₁₈
<i>n</i> - α -olefins	97.0	96.5	97.5	96.5	96.0	96.0	96.0
branched olefins	1.0	1.0	1.0	2.0	2.5	3.0	3.0
β -internal olefins	2.2	2.4	1.0	1.5	1.5	1.5	1.5
paraffins	0.1	0.1	0.1	0.05	0.05	0.05	0.05
conjugated dienes	0.1	0.1	0.1	0.05	0.05	0.05	0.05
aromatics	0.1	0.1	0.1	0.05	0.05	0.05	0.05
total monoolefins	99.9	99.9	99.9	99.9	99.9	99.9	99.9

TiCl₄/EtAlCl₂ have been patented as catalysts for the industrial ethylene oligomerization processes.⁸³ In this case the following conditions must be maintained: 20–30 atm, 353–363 K, and toluene as a solvent. After a 1-h reaction 515 kg of α -olefins (18% C_{4–6}, 30% C_{8–10}, and 38% C_{12–18}) per kilogram of Zr are obtained. For the titanium catalyst, the product consists of 18% C_{4–6}, 42% C_{8–10}, and 35% C_{12–18} α -olefins (102 kg (kg of Ti)⁻¹ h⁻¹) when the reaction was carried out at 293–313 K under 20–25 atm. The C_{4–6} fraction recycled with unreacted ethylene resulted in an increase of the desirable C_{12–18} fraction to 93–96%, with the content of α -olefins reaching 95% in the final products. Also zirconium catalytic systems described in the Idemitsu patents are a base for commercial use.^{230–232}

IV. Oligomerization of Propylene

The propylene oligomerization literature is considerably poorer than for the ethylene oligomerization. The catalysts of oligomerization of propylene and conditions of this reaction are summarized in Table VII.

Most of these catalysts are also active in the ethylene oligomerization (they were partly discussed earlier). Also in this case the titanium, zirconium, and nickel complexes are the most popular catalysts. Propylene oligomers are more structurally diverse than ethylene oligomers (see Scheme VIII). The propagation step of the propylene oligomer growth in presence of transition-metal complexes occurs through four intermediates, wherein propylene inserts into the metal–hydrogen and metal–alkyl bonds. Also, in the chain-termination reaction (Scheme VIII) β -hydrogen can be eliminated from CH₃, CH₂, or CH groups of the oligomer chain. All these possibilities give rise to various olefin isomers.

IV.1. Transition-Metal Complexes as Catalysts of Propylene Oligomerization

IV.1.1. Titanium

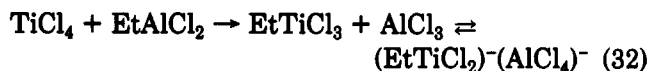
Propylene shows outstanding inclination toward the cationic oligomerization. Therefore, the acidic system TiCl₄/EtAlCl₂ oligomerizes propylene to irregular strongly branched olefins.² A change of the chlorine atoms, in this system whether the one next to titanium or aluminum for the donor ligands, e.g. C₂H₅O, leads to yield of linear olefins.² Both actions increase the electron density in the titanium ion and linearity of obtained oligomers.

Investigations of the TiCl₄/EtAlCl₂ system during the cooligomerization of ethylene with propylene indicated that, depending on the reaction temperature and solvent, anionic–coordination and cationic centers coexist.

TABLE VI. Oligomers Composition of the Gulf, Ethyl, and SHOP Processes⁷⁷

	Gulf	Ethyl	SHOP
α -olefins	91.0–97.0	63.0–97.5	96.0–97.5
branched olefins	1.6–78.0	1.9–29.1	1.0–3.0
internal olefins	–	0.6–8.2	1.0–2.4
paraffins	1.4	0.1–0.8	0.1
total monoolefin	98.6	99.0	99.9

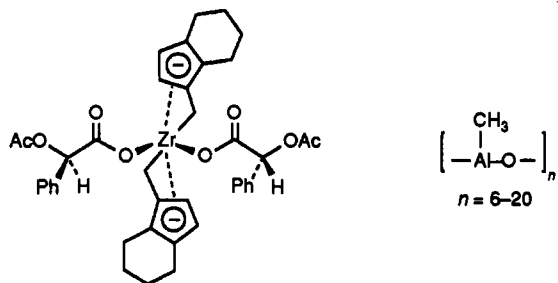
AlCl₃ formed as a product of the TiCl₄ alkylation or a reaction of EtAlCl₂ with halogenohydrocarbon solvent^{25,28} (reactions 32⁶¹ and 33) can form the cationic



center for propylene oligomerization. It is assumed that the TiCl₄/EtAlCl₂ system oligomerizes olefins to a lesser or greater degree according to a cationic mechanism, in which the oligomer chain has a positive charge and forms an ionic pair with a negative counterion, e.g. AlCl₄⁻.⁶¹ A decrease in the Ti(IV) ion electron affinity decreases its acidity and increase a coordination mechanism contribution in the whole oligomerization reaction, which in turn causes an increase of the product linearity. During the investigations of the propylene oligomerization in the presence of the TiCl₄/*i*-Bu₂AlCl system in toluene it was proved that the solvent participated in the oligomer chain termination reaction as the chain-transfer agent. This is the reason why a part of the obtained product has oligomers with toluene moiety as end groups.⁸⁴

IV.1.2. Zirconium

Propylene oligomers have different lengths depending on the kind of the zirconium catalyst used. In presence of the Zr(acac)₄/Et₃Al₂Cl₃/R₃P (R = alkyl or aryl) system, low molecular C_{6–9} oligomers are obtained.⁸⁵ When the system bis(pentamethylcyclopentadienyl)-dichlorozirconium activated with methylaluminumoxanes⁸⁶ is used, longer chain oligomers, having more than C₁₆ in the chains, are found in the products. (*S*)-[1,1'-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium bis(*O*-acetyl-*R*-mandelate) activated with methylaluminumoxane (see below) is a stereospecific catalyst of the propylene and 1-butene oligomerization.²⁰³



The Zr–CH₃ bond is the active center of zirconium catalysts. It is formed in the methylation reaction of the zirconium ions in the complexes with e.g. methylaluminumoxanes. The next steps of the catalyst action are olefin complexation and olefin insertion into the Zr–C–H₃ bond (reaction 34). The chain termination reaction

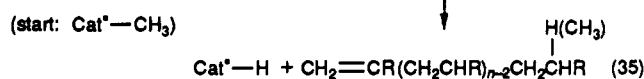
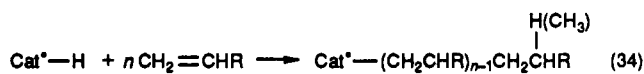
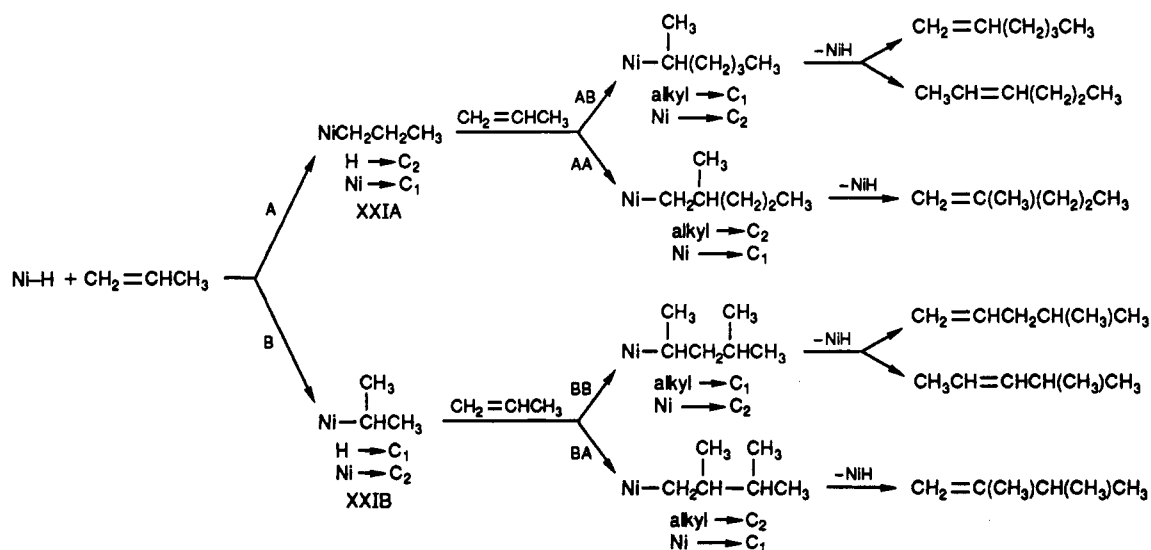
TABLE VII. Oligomerization of Propylene

catalyst	react condn	products	yield	ref(s)
$\text{TiCl}_4/\text{R}_2\text{AlCl}$ (Al/Ti = 0.69), R = C_2H_5 , $i\text{-C}_4\text{H}_9$	Titanium toluene, 60 °C, 15 min	olefins $\bar{M}_n = 92$ (27%), 131 (36%), 163 (35%), 382 (2.7%)	conv = 95%, 430×10^{-3} L (g of TiCl_4) ⁻¹ min ⁻¹ ethylene with propylene conv = 90%	25, 84
$\text{TiCl}_4/(\text{C}_2\text{H}_5)_2\text{Al}/\text{RCl}$ (Al/Ti = 10), R = alkyl $\text{TiCl}_4/(\text{ONi})_2(\text{OH})_n/\text{C}_2\text{H}_5\text{AlCl}_2$, n = 1, 2, 3	hexane, 40 °C, 15 min	oligomers $\text{C}_6 = 65\%$, $\text{C}_9 = 25\%$, $\text{C}_{12} = 8\%$, $\text{C}_{15} = 2\%$		163 331
$\text{TiCl}_4/\text{Ti}(\text{OBu})_4/\text{Zr}(\text{OBu})_4/(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3$ (1:2:1:10)	hexane/toluene, 80 °C, 2 h	α -olefins = 72% of the product $\bar{M}_n = 114$	conv = 86% (129 g), PP = 2 g	87
$(\text{C}_2\text{H}_5\text{O})_2\text{TiCl}_2/\text{C}_2\text{H}_5\text{AlCl}_2$	benzene, 5 °C	olefins $\bar{M}_{\text{av}} = 340$, linearity = 49%		332
$\text{Zr}(\text{acac})_4/(\text{C}_2\text{H}_5)_2\text{Al}_2\text{Cl}_3/\text{PR}_3$ (Al/Zr = 10-20:1) $\text{Zr}(\pi\text{-allyl})\text{Br}_3/(\text{PhCH}_2)_2\text{ZrBr}_3/(\text{C}_2\text{H}_5)_2\text{Al}_2\text{Cl}_3$ (AcO)Ph(CHCOO) ₂ Zr(1,1'-ethylenbis(4,5,6,7-tetrahydro-1-indenyl))/methylaluminoxane $[\eta^5\text{-C}_6(\text{CH}_3)_5\text{ZrCl}_2/\text{methylaluminoxane}$, n = 6-20	Zirconium 100-600 psig, 150 °F toluene, 50 °C 8 atm, 50 °C, 4 h	olefins C_{6-9} α -olefins C_8 and C_{9-6} olefins $\text{C}_{9-21} = 53\%$ oligomers $\text{C}_9 = 15.5\%$, $\text{C}_{12} = 5.9\%$, $\text{C}_{>15} = 78.5\%$	conv = 60%	85 238 203 86
$\text{C}_2\text{H}_5\text{NiP}(\text{OC}_2\text{H}_4\text{R-}o)_2/\text{H}_2\text{SO}_4$, R = alkyl, alkoxy C_{1-3} $(\pi\text{-C}_3\text{H}_5)\text{NiBr}/(\text{C}_6\text{H}_{11})_3\text{P}/\text{C}_2\text{H}_5\text{AlCl}_2$ $(\pi\text{-C}_3\text{H}_5)_2\text{Ni}/\text{SiO}_2/\text{Al}_2\text{O}_3/\text{SiO}_2/\text{CH}_3\text{AlCl}_2$ (Al/Ni = 1:4, Ni/OH = 1)	Nickel haloaromatic, 0-50 °C -75 and +55 °C -40 and +50 °C, 2.5 h, propylene flow rate = 360 cm ³ /min -14 and +40 °C, propylene flow rate = 360 cm ³ /min <i>n</i> -heptane, 40 °C 90-380 psig, 150 °F, 3 h 145 °F, 3 h	oligomers olefins $\text{C}_{>12} = 10-15\%$ olefins $\text{C}_6 = 25-67\%$, $\text{C}_9 =$ 17-43%, $\text{C}_{12} = 14-32\%$ olefins $\text{C}_6 = 40.5\%$, $\text{C}_9 =$ 56%, $\text{C}_{12} = 3.5\%$ oligomers branched olefins C_9 , C_{12} olefins $\text{C}_{>9} = 40\%$ oligomers $\text{C}_{>12} = 21\%$ olefins $\text{C}_6 = 62\%$, $\text{C}_9 = 25\%$	conv = 99 conv = 80%	253 333 96-99 98
$(\pi\text{-C}_3\text{H}_5)_2\text{Ni}/\text{Al}_2\text{O}_3/\text{SiO}_2$ (Ni/OH = 1) $(\pi\text{-C}_3\text{H}_5)_2\text{NiCl}/\text{Lewis acids}$ $\text{Ni}(\text{RCOO})_2/(\text{C}_2\text{H}_5)_2\text{AlCl}$, RCOO = octanoate, oleate $\text{Ni}(\text{acac})_2$ supported on $\text{SiO}_2/(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3/\text{Ph}_3\text{PCl}_n$, n = 0, 1 $\text{Ni}(\text{acac})_2$ supported on $\text{Al}_2\text{O}_3/\text{SiO}_2/(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3/\text{Ph}_3\text{P}$ or Bu_3P (Al/Ni = 3) $\text{Ni}(\text{acac})_2$ supported on $\text{Al}_2\text{O}_3/\text{SiO}_2/(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3$	toluene, 1-100 atm, 0-130 °C 40-80 °C toluene, 75 °C, 0.75 h chlorobenzene chlorobenzene, 110 psig, 60 °C, 20 h	oligomers $\text{C}_{>12} = 21\%$ olefins $\text{C}_6 = 62\%$, $\text{C}_9 = 25\%$ olefins $\text{C}_6 = 77\%$, $\text{C}_9 =$ 17%, $\text{C}_{12} = 3\%$ oligomers $\text{C}_6 = 59\%$, $\text{C}_9 =$ 32%, $\text{C}_{12-16} = 9\%$ oligomers oligomers $\text{C}_{6-9} = 73\%$, $\text{C}_{12-18} = 18\%$, $\text{C}_{>21} = 9\%$	38 g (mol 439 Ni) ⁻¹ h ⁻¹ 2384 mol of C_3^{2-} (mol of Ni) ⁻¹ h ⁻¹ (80 °C) conv = 73%, 7220 mol C_3^{2-} (mol of Ni) ⁻¹ linearity = 80%	93, 94, 154, 439 95
$[\text{CH}(\text{CF}_3)\text{O}]_2\text{Ni}/(\text{C}_2\text{H}_5)_2\text{Al}(\text{OEt})$ (COD)Ni[CH(C(CF ₃)O) ₂]	toluene, 700 lb/sq, 35-50 °C 40-150 °C	olefins $\text{C}_{>6} = 20\%$ oligomers	conv = 88, 7-99.8%	159 372
$\text{Ni}(\text{acac})(\text{Bu}_3\text{P})\text{Cl}/(\text{C}_2\text{H}_5)_2\text{AlCl}$ NiX_2 or $\text{PdX}_2/(\text{C}_2\text{H}_5)_2\text{AlCl}$ or NaBH_4 , X = -SR, -CRC(SR)-, $\text{RSC}_6\text{H}_4\text{F}$, e.g., $\text{C}_6\text{F}_5\text{OH}/\text{NiOAc}$, $4\text{H}_2\text{O}/\text{Et}_2\text{AlCl}$ $\text{NiCl}_2\text{H}_2\text{O}/\text{alumina spheres}/(\text{C}_2\text{H}_5)_2\text{AlCl}$	chlorobenzene chlorobenzene, 110 psig, 60 °C, 20 h	oligomers $\text{C}_{6-9} = 73\%$, $\text{C}_{12-18} = 18\%$, $\text{C}_{>21} = 9\%$	linearity = 80%	341 206
Ni/microfibrous carbon fibers/haloalkylaluminum	toluene or cyclohexane -30 and +20 °C cyclohexane, 293 K cyclohexane, 298 K	oligomers high oligomers high branched oligomers		100 62 102
$\text{Lu}[\eta^5\text{-C}_6(\text{CH}_3)_5]_2\text{CH}_3/(\text{C}_2\text{H}_5)_2\text{O}$ $[\eta^5\text{-C}_6(\text{CH}_3)_5]_2\text{MH}_2$, M = La, Nd $[(\text{CH}_3)_2\text{Si}(\eta^5\text{-C}_6(\text{CH}_3)_5)_2\text{LuH}]_2$				

(α -C ₃ H ₇)Ru(CO) ₃ X	Ruthenium	high branched oligomers	62
R _n AlX _{3-n} /chlorohydrocarbon, n = 1, 2, 3; R = hydrocarbyl, RO, RC(=O)-; halogen R ₃ Al or R ₂ AlH; R = alkyl C ₂₋₁₈	Aluminum	oligomers $\bar{M}_n = 592$ α -olefins C ₇₋₉ = 25%, C ₁₀₋₁₄ = 37%, C ₁₆₋₁₈ = 19% (branched)	343 367
BF ₃ /H ₃ PO ₄ , BF ₃ /HPO ₃ , BF ₃ /H ₄ P ₂ O ₇ BF ₃ /ROH, R = CH ₃ , C ₄ H ₉	B, Al, Ti, and Zn Halides Systems	oligomers C ₉₋₁₈ oligomers C ₁₂ oligomers C ₁₂₋₃₀	125-127 128-130
BF ₃ /HF BF ₃ /H ₂ O	influence of solvent on oligomer yield: C ₂ H ₄ Cl ₂ > PhNO ₂ > CCl ₄		350 136
BF ₃ /polyolefins (0.2-0.4%) BF ₃ /ZSM-5 (SiO ₂ /Al ₂ O ₃ = 70)	5 atm, 100 °C, 60 min 40 °C 150 °C	oligomers C ₁₂₋₁₅ oligomers C ₁₂₋₁₈ = 72%, C _{>20} = 9% oligomers C ₁₉₋₂₀ oligomers C ₄₋₉ = 28.7%, C ₇₋₁₀ = 55% without aromatic hydrocarbons	351
BF ₃ /TiO ₂ AlCl ₃ AlCl ₃ /CH ₃ C ₃ H ₅ /C ₂ H ₄ Cl ₂ (1:3.5:2.5) AlCl ₃ /graphite AlBr ₃ , AlBr ₃ /HBr TiCl ₃ TiF ₄ /Al ₂ O ₃ ZnCl ₂	70 °C 600 psig, 200 °C -50 and +100 °C 95-315 °C 300 °C	oligomers C ₆₋₂₄ oligomers $\bar{M}_n = 1074$ oligomers C ₉ oligomers mainly oligomers C ₉	349 131 364 359 352-354 356 330 132-134
H ₃ PO ₄ H ₃ PO ₄ /SiO ₂ H ₃ PO ₄ (65%)/SiO ₂ (1.5:1)	H ₃ PO ₄ Acid and Others	oligomers olefins C ₉ = 60-80% oligomers C ₆ = 25%, C ₉ = 55%, C _{>12} = 20% oligomers C ₁₂ = 75% oligomers C ₈ = 6%, C ₉ = 56%, C ₁₂ = 36% oligomers C ₉₋₁₂ oligomers C ₁₂₋₁₆	346 105 107-109
H ₃ PO ₄ /SiO ₂ (P ₂ O ₅ = 36.1%) H ₃ PO ₄ /SiO ₂ /graphite H ₃ PO ₄ /SiO ₂ H ₃ PO ₄ /Al ₂ O ₃ /SiO ₂ or Al ₂ O ₃ H ₄ P ₂ O ₇ /SiO ₂ /NaA zeolite HF H ₂ SO ₄ mineral acids	30-80 atm, 183-230 °C 220 °C two-step process 180 °C 400-0 psig, 20-30 °C 25 °C 205-315 °C	0.155 mol (g of catalyst) ⁻¹ h ⁻¹ high conversion, traces of PP oligomers C ₁₂ oligomers C ₇₋₁₄ oligomers conv = 99%	104 110 362 113 347 348 105 344
CuP ₂ O ₇ Cu/Zr/aluminum phosphate	Inorganic Oxides Systems	oligomers C ₅₋₁₂	367 375
TiO ₂ /SiO ₂ Al ₂ O ₃ /SiO ₂ /MoO ₃ , WO ₃ , Cr ₂ O ₃ , NiO, FeO, or ZnO MoO ₃ /Al ₂ O ₃ 10% NiO/Al ₂ O ₃ /SiO ₂	oligomers oligomers C ₁₀₋₁₈ , max C ₁₃ oligomers C ₆ = 24%, C ₉ = 48%, C _{>10} = 42%		355 358 324 149

TABLE VII (Continued)

react condtn	products	yield	ref(s)
<p>$\text{TiO}_2/\text{ZrO}_2/\text{Ni}$ (0.1%) sulfided Ni/mica/montmorillonite (N-SMM) Ni/HZSM-5 Ti/Al/silicalite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 161$, $\text{SiO}_2/\text{TiO}_2 = 46$) $\text{SiO}_2/\text{Fe}_2\text{O}_3(573)$, $\text{SiO}_2/\text{TiO}_2(46)$ (Ti, Fe silicalite) ferrites $\text{M}_{x/n}(\text{TO}_2)_x(\text{SiO}_2)_{3x-1}$, M = cation, T = B, Al, Fe(III); x = 0.05–6.6; n = valence of M, (1.25% F)</p>	<p>oligomers $\text{C}_{>10} = 72.8\%$ oligomers C_{12-21} oligomers C_{9-16}, max C_{6-9} oligomers, $\text{C}_{>7} = 54\%$ oligomers $\text{C}_{>8} = 35\%$ oligomers $\text{C}_{6-9} = 35\%$, $\text{C}_{10-17} = 62.4\%$, $\text{C}_{>18} = 2.6\%$</p>	<p>conv = 98%</p>	<p>148, 371 370 142, 303 365 366 373</p>
<p>zeolites</p>	<p>branched oligomers</p>	<p>branched oligomers in the product decreases in order: $\omega > \text{HY} > \text{mordenite} \geq \text{ZSM-5} > \text{offretite} > \text{boralite}$</p>	<p>138</p>
<p>zeolites: H, NaHY, NaMgY</p>	<p>oligomers, aromatics</p>		<p>137, 144, 145, 204, 328 149</p>
<p>zeolite NaX/30%Ni(III)</p>	<p>oligomers $\text{C}_8 = 24\%$, $\text{C}_9 = 57\%$, $\text{C}_{12} = 19\%$</p>	<p>conv = 62%</p>	
<p>KO-10/4 zeolite 25 M</p>	<p>oligomers C_{9-12} oligomers C_{3-11}</p>	<p>conv = 99% conv = 95%</p>	<p>140 360</p>
<p>HZSM-5</p>	<p>oligomers C_{9-16} olefins, aromatic hydrogen, paraffins</p>		<p>222</p>
<p>HZSM-5</p>	<p>oligomers C_{6-20}</p>		<p>36, 71, 72, 141, 202 368</p>
<p>zeolite Y (dealuminated, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 75$)</p>	<p>oligomers bp = 330 °F (19.8%), bp = 330–650 °F (64.3%), bp > 650 °F (9.1%)</p>		
<p>ZSM-23/trialkylpyridine or organophosphate HZSM-12</p>	<p>oligomers $\text{C}_{>12}$ oligomers $\text{C}_9 = 59\%$, $\text{C}_{12} = 27\%$, $\text{C}_{18} = 8.7\%$</p>	<p>0.25 g g⁻¹ h⁻¹ conv = 61–99%</p>	<p>369, 446 442</p>
<p>zeolites (ZSM-5, boralites, offretite-HY, mordenite, or omega)/20% sepiolite SiO_2</p>	<p>oligomers $\text{C}_{6-12-12}$, low selectivity oligomers</p>		<p>374 88</p>

SCHEME VIII. Reaction Paths of Propylene Oligomerization in the Presence of a Nickel Catalyst⁸¹

occurs as a result of the β -hydrogen elimination reaction and the Zr-H bond restoration (reaction 35).²⁰³

The mixed systems consisting of titanium and zirconium halides and alkoxy (Ti:Zr = 3-1:1) modified with $\text{Et}_3\text{Al}_2\text{Cl}_3$ exhibit high activity in the linear propylene α -oligomerization. The products of this reaction contained, beside high molecular oligomers, polypropylene. The propylene conversion was in the range of 78-93%.⁸⁷

IV.1.3. Nickel

The structures and mechanisms of the nickel complexes action in the propylene oligomerization are the same as in the ethylene oligomerization. The bonds Ni-H and nickel-alkyl are the active centers of the catalysts. The catalytic propylene oligomerization begins with olefin insertion into the Ni-H bond Scheme VIII. Hydrogen from the Ni-H bond can be bonded to the carbon C₁ or C₂ forming, respectively, branched or linear alkyl groups bonded to the nickel ion. These alkyl groups can migrate to the propylene molecule in two modes: to the propylene carbons C₁ or C₂. These possibilities are responsible for the branched products. It is possible however to control these reactions with the help of the phosphine ligands,^{51,54} as it occurs in the system $[(\pi\text{-C}_3\text{H}_5)_2\text{NiBr}]_2/\text{Et}_3\text{Al}_2\text{Cl}_3/\text{L}$ where L = PMe_3 , PEt_3 , PBu_3 , $\text{P}(i\text{-Pr})_3$, PCy_3 , and $\text{P}(t\text{Bu})_2(i\text{-Pr})$. Only very bulky $\text{P}(t\text{Bu})_2(i\text{-Pr})$ changes the first step of the oligomerization—propylene insertion into the Ni-H bond from the iso mode—the Markovnikov mode insertion product XXIB - into 1-propyl mode - to the anti-Markovnikov insertion product XXIA (Scheme VIII, path B and A, respectively). More bulky phosphine ligands favor less volume branched alkyl in the formed nickel-alkyl group during the olefin insertion reaction. In this situation nickel ion's bonding to the C₂ carbon of the propylene molecule is blocked. Thus,

when nonbulky phosphines, PMe_3 , PEt_3 , or $\text{P}(n\text{-Pr})_3$, were used as the ligands highly branched oligomers were the products of the propylene oligomerization.

Detailed investigations^{1,54} of this kind of catalysts have unequivocally established that the phosphine influence on the oligomer structure has steric, not electronic character. More bulky phosphines in these catalysts are responsible for formation of more linear oligomers.

Generally, nickel complexes do not oligomerize propylene to higher molecular weight olefins. Mainly dimers and trimers are the products of this reaction.

Highly branched oligomers, dimers, and trimers are obtained when the system nickel octanoate/ EtAlCl_2 is used as a catalyst.⁸⁹ The same product composition but with linearity of 50-70% was obtained by using (η^4 -cycloocten-1-yl)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)nickel without cocatalysts.⁵³ Modification of this catalyst with Et_2AlOEt ⁹⁰ or $(i\text{-Bu})_2\text{AlH}$ ⁹¹ raised the catalyst's activity but without a change of product's composition. In this type of nickel catalyst, activity of olefin oligomerization increases with acidity of organoaluminum compounds and decrease of β -ketone ligand donor properties. Chevron Research reported a catalyst prepared by contacting Ni or Pt salt with a fluoroorganothiols or sulfide followed by addition of organoaluminum halide or alkoxide or borohydride. For example, the bis(pentafluorophenylthiolato)nickel/ Et_2AlCl catalyst system gives high yield of propylene oligomers (C₆₋₉, 70%) having $\geq 80\%$ linear olefins.²⁰⁶

C₉ (40%) and higher propylene oligomers were the products of oligomerization reaction in presence of heterogenized catalyst $\text{Ni}(\text{acac})_2/\text{Et}_3\text{Al}_2\text{Cl}_3/\text{Al}_2\text{O}_3\text{SiO}_2$.⁹²⁻⁹⁵

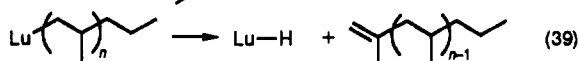
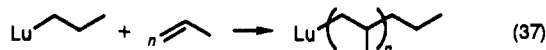
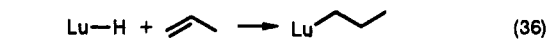
By changing the alumina-silica gel composition in the heterogenized π -allyl nickel systems it was possible to oligomerize propylene without organoaluminum compounds as cocatalysts. This catalytic activity was exhibited in supports containing 50% by weight Al_2O_3 to 70% by weight Al_2O_3 . Modification of all these systems with chloroalkylaluminum compounds, TiCl_4 , or AlBr_3 gave highly active catalysts for propylene oligomerization in the flow system.⁹²⁻⁹⁵

Hydrated iron group metal salts supported on porous

carriers after drying and calcination modified with organoaluminum compounds are used as catalysts in Huels-UOP—"Hexall" and "Octol" processes for propylene oligomerization and propylene-butene copolymerization mainly to dimers 60%. These reactions are carried out at 35–50 °C, 700 psig. The most effective catalysts contain nickel surface complexes.^{159,161,162} Ni(NO₃)₂ or NiCl₂·2H₂O on alumina spheres calcined and activated with Et₂AlCl or AlCl₃ oligomerizes propylene to dimer (80%) and higher oligomers (20%).¹⁵⁹ The calcination temperature affected the catalyst selectivity.¹⁵⁹

IV.1.4. Various Metals

Lutetium complexes: (η^5 -C₅Me₅)₂LuCH₃·ether (XXII),¹⁰⁰ [(η^5 -C₅Me₅)₂LuH]₂ (XXIII),¹⁰¹ and [(CH₃)₂Si(η^5 -C₅Me₅)₂LuH]₂ (XXIV)¹⁰² are catalytically active in the propylene oligomerization. The complex XXIV is 10-fold more active than the XXIII. The oligomers having more than 21 carbons in their chains were products of these system. The propylene oligomerization mechanism in such catalysts is similar to that described for other transition-metal complexes. It proceeds in the following way:



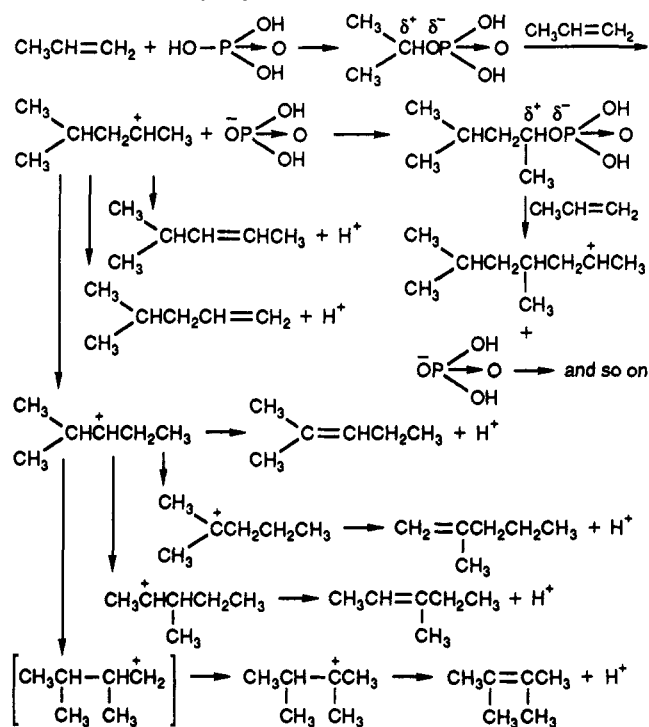
The oligomer chain termination step occurs thanks to the olefin metalation, β -hydrogen elimination, and β -methyl group elimination (reactions 38, 39, and 40, respectively).

(π -CH₂=CH-CH₂)Ru(CO)₃X (X = Br, Cl) oligomerizes propylene to highly branched C_{9–15} oligomers.⁶²

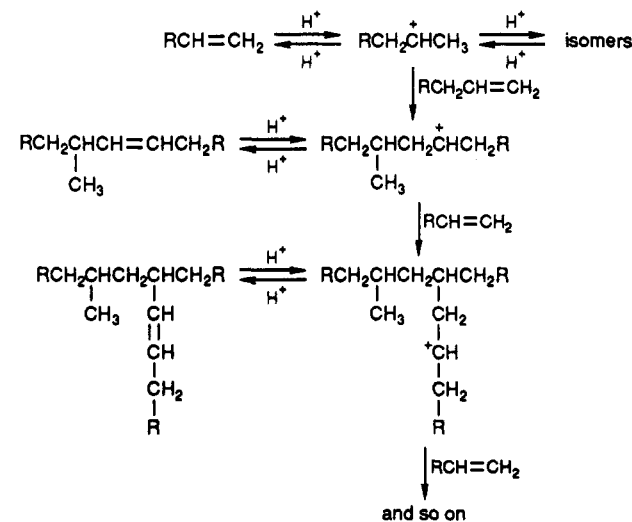
IV.2. Cationic Oligomerization of Propylene

In 1933 Universal Oil Products Co. developed the supported catalytic system H₃PO₄/SiO₂ for propylene oligomerization.¹⁰³ Amount of supported phosphoric acid is of the range 62–65% by weight. Also, asbestos can be used as carrier in this reaction. Use of neutral carrier such as active carbon leads to the formation of alkyl phosphates which volatilize from the catalyst bed. Thus H₃PO₄ is removed from the catalytic system. This does not occur when acidic carriers are used. Silica,^{104–110} kaolin,¹¹¹ silicon, silicon carbide, marble, glass, quartz,¹¹² and alumina-silica¹¹³ were investigated as supports of H₃PO₄. Also, some processes for propylene oligomerization using only H₃PO₄ as a catalyst have been described.^{114,115} The reaction mechanism for kind of oligomerization is presented in Scheme IX. Dimers, trimers, and tetramers are found when the reaction is carried out at lower temperatures (520 K). At higher temperatures longer chain oligomers are formed. Propylene hydropolymerization reactions, yielding paraffins, begin to occur when the reaction temperature is

SCHEME IX. Mechanism of Propylene Oligomerization in the Presence of H₃PO₄ as a Catalyst¹⁰⁴



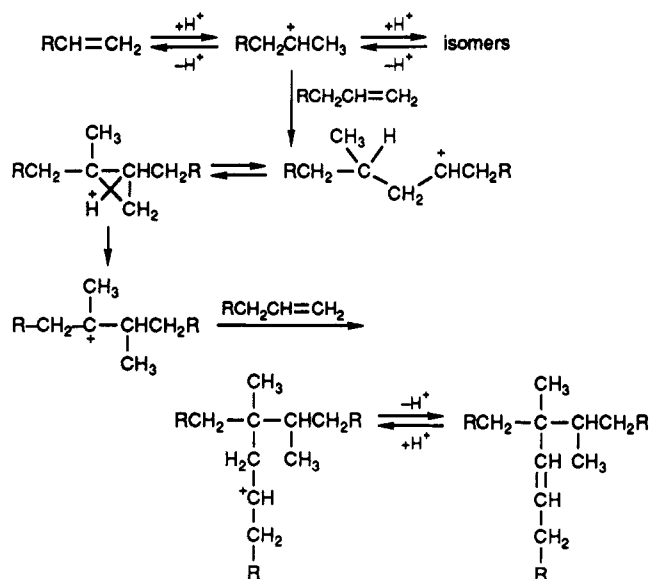
SCHEME X. Cationic Mechanism of α -Olefin Oligomerization in the Presence of the System BF₃/n-BuOH¹²⁶



higher than 580 K. The addition of steam to the reaction mixture at this temperature reduces the paraffin content in the products. The molecular weight of oligomers grows when the reaction pressure is raised.

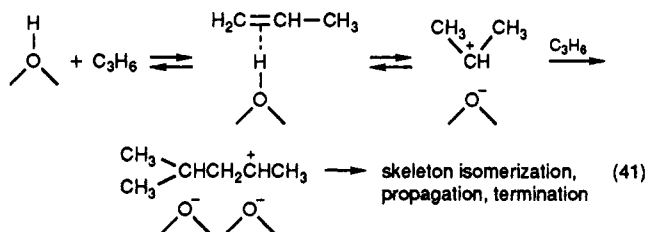
Repas¹⁰⁴ has proved that addition of water to the system H₃PO₄/SiO₂ increased the propylene oligomerization product yield. He has also proposed a mechanism for this reaction in which surface propylene phosphate esters are the catalytic centers for propylene oligomerization. This catalytic system is often modified with cupric,^{116–118} nickel,^{117,121} and calcium¹¹⁶ salts, manganese derivatives,¹²² and amines.^{123–124}

Many other acidic catalysts possessing a Lewis acid as a component are active in propylene oligomerization. The most popular are BF₃/H₃PO₄,^{125–127} BF₃/H₂O,^{128,136} BF₃/MeOH,¹²⁹ BF₃/BuOH,¹³⁰ AlCl₃,¹³¹ and ZnCl₂,^{132–134}

SCHEME XI. Shubkin's Mechanism of Cationic α -Olefin Oligomerization in the Presence of a Lewis Type Catalyst¹³⁶

and they are listed in Table VII. The cationic mechanisms of propylene oligomerization in presence of Lewis acids are in Schemes X and XI. In this case, an increase in reaction temperature causes a decrease in oligomer molecular weight.¹³⁶

Propylene oligomerization in presence of alumina-silica gels and zeolites, e.g. HNaY,¹³⁷ are initiated on the surface of acidic Brønsted type sites after propylene adsorption. An increase in the amount of the acidic

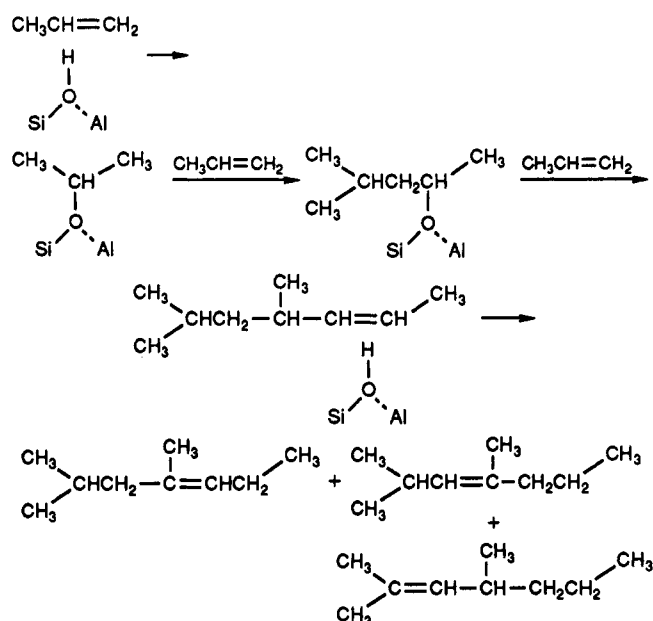


centers on the carrier surface and their acidic strength results in increasing of the propylene oligomerization rate and greater branching of the product. The oligomer chain branching depends on the carrier porosity. The following order of decreasing branching with pore size was established for zeolites: omega > HY > mordenite > ZSM-5 > offretite > boralite.¹³⁸⁻¹⁴³ Omega with the largest (10 Å) pore opening gives the most branched oligomers.

In the presence of these catalysts mainly low molecular weight oligomers are formed. Some paraffins and aromatics are formed as products of the side reactions, namely, isomerization, cracking, aromatization, and hydrogen transfer.

The propylene oligomerization on HY zeolites at 213–313 K occurs through surface alkoxy derivatives formed in the reaction between protonated alkenes and surface oxygens of the zeolite. Carbocations are not intermediates in this case. The mechanism of this reaction is presented on Scheme XII.²⁰⁴

A point of some interest in propylene oligomerization is the selective poisoning of sites on the outside of zeolite HZSM-23 particles with trialkylpyridine or organo phosphite compounds having an effective cross

SCHEME XII. Mechanism of Propylene Oligomerization in the Presence of Zeolite HY²⁰⁴

section larger than that of the pores. In this case propylene is oligomerized in zeolite pores, improving in this way linearity of product.^{369,446}

The following systems have been described as catalysts of propylene oligomerization: MoO₃/Al₂O₃,¹⁴⁶ TiO₂/ZrO₂/Ni,¹⁴⁸ NiO/Al₂O₃/SiO₂,¹⁴⁹ and Fe, Co, and Ni oxides on alumina/silica.^{147,150,151}

V. Oligomerization of Higher α -Olefins

The dimerization and trimerization of higher olefins are classified in this article as the oligomerization reactions. The catalytic systems for higher α -olefin oligomerizations are presented in Table VIII. Olefin reactivity, in this reaction, decreases in the following order: ethylene > propylene > 1-butene > 1-hexene > 1-octene > 1-decene.^{53,58} Longer chain α -olefins undergo a more difficult oligomerization reaction than ethylene and propylene. The selectivity of this reaction in the case of higher α -olefins is lower. This is a result of the fact that higher α -olefins can form a greater amount of isomers than ethylene and propylene in the oligomerization cycle as is shown in Scheme XIII. Catalysts similar to that used for ethylene or propylene oligomerization can be used for higher α -olefin oligomerization. Among the most popular are titanium, zirconium, and nickel complexes, homogeneous and heterogenous Lewis and Brønsted acids, and inorganic oxides.

V.1. Organometallic Complexes as Catalysts of Higher α -Olefin Oligomerization

V.1.1. Titanium and Zirconium

The system TiCl₄/R_nAlCl_{3-n} ($n = 1, 2, 3$; R = alkyl) oligomerizes 1-hexene.¹⁶⁸ Modification with halogeno-hydrocarbons, phosphoro- and sulfuroorganic compounds, alkali metal hydrides, and nickel salts gave reactive catalysts in the 1-decene,¹⁶³ CH₂=CH-(CH₂)_nCH₃ ($n = 1-5$),¹⁶⁴ C₆₋₁₄ α -olefin,¹⁶⁵ and C₃₋₆ α -olefin¹⁸⁷ oligomerization.

TABLE VIII. Oligomerization of Higher α -Olefins

catalyst	olefin/react condtn	products	yield	ref(s)
$\text{TiCl}_4/(\text{C}_2\text{H}_5)_2\text{AlCl}_n/3\text{RCl}$, $n = 0, 1, 1.5$	Titanium olefins $\text{C}_{3-14}/42^\circ\text{C}$, 15 min, hexane	oligomers C_{36-360}	conv = 90%	163
$\text{TiCl}_4/(\text{C}_2\text{H}_5)_2\text{Al}_2\text{Cl}_3$	1-hexane/ 30°C , toluene	vinyldiene olefins = α -olefins = 5.3%; $\bar{M}_w = 186$ oligomers, index viscosity = 131, flash point = 210°C	conv = 38.5%	168
$\text{TiCl}_4/\text{AlCl}_3/\text{LiH}$	1-butene, 1-octene/ $100-120^\circ\text{C}$	oligomers		165
TiCl_4/Ni (salt)/organoaluminums (2-20:1-5:5-86)	α -olefins $\text{C}_{2-8}/20-180^\circ\text{C}$, contact time = 0.1-34 s $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CH}_3$, $n = 1-5$	oligomers		167
$\text{TiCl}_4/\text{P}_2\text{S}_5\text{N}$ -hydrocarbons/ $\text{R}_3\text{Al}_2\text{Cl}_3$, RAlCl_2 (1:0.1-4:1-5)	1-decene/ 80°C , 4 h 1-octene/hexane	oligomer $\bar{M}_n = 356$ olefins $\text{C}_{24} = 65\%$	conv = 86% conv = 80%	164
$\text{TiCl}_4/(\text{OBu})_4/\text{Zr}(\text{OBu})_4/(\text{C}_2\text{H}_5)_2\text{Al}_2\text{Cl}_3$ (1:2:1:10) $\text{TiCl}_4/\text{propylene oxide}/(\text{C}_2\text{H}_5)_2\text{Al}_2\text{Cl}_3$ (Al/Ti = 1.25)				87 170
$\text{Cp}_2\text{ZrCl}_2/(\text{CH}_3)_2\text{Al}/\text{H}_2\text{O}$	Zirconium 1-hexene/ 10 psig , 20°C , toluene	oligomers $\text{C}_{30-60} = 45-51\%$	conv = 93%	392
$\text{ZrCl}_4(\text{HFCl}_2)/\text{AlCl}_3$ (Al/Zr = 1)	1-decene/ 99°C , 1 h, heptane			169
$\text{Ni}(\text{CF}_3\text{COCHCOCF}_2)_2$, $(\text{C}_2\text{H}_5)_2\text{Al}_2\text{Cl}_3/\text{Ph}_3\text{P}$ or $\text{Ni}(\text{CF}_3\text{COCHCOCF}_2)_2/(\text{C}_2\text{H}_5)_2\text{AlOCC}_2\text{H}_5$ $\text{Ni}(\text{COD})(\text{CF}_3\text{COCHCOCF}_2)_2$	Nickel 1-butene (isomerization of 1-C ₄ to 2-C ₄) 1-butene, 2-butene, 1-hexene, 1-octene/ 70°C , 0.5-2 h	olefins $\text{C}_8 = 78\%$, $\text{C}_{12} =$ 17.6%, $\text{C}_{16} = 4.4\%$ dimers and trimers, linearity = 36-85%	conv = 31.3% 62-330 mol olefins (mol of Ni) ⁻¹ h ⁻¹	153, 379 53, 55
$\text{Ni}(\text{HCOO})_2/(\text{C}_2\text{H}_5)_2\text{Al}$ (Al/Ni = 40) $\text{Ni}(\text{acac})_2/(\text{C}_2\text{H}_5)_2\text{Al}_2\text{Cl}_3/\text{Ph}_3\text{P}$ or not	1-hexene/ 60°C , 4 h, toluene 1-hexene/ 60°C , 4 h, toluene	α -olefins = 89%, $\bar{M}_w = 174$ α -olefins = 50%; $\bar{M}_w =$ 172-271	conv = 38.3% conv = 63%, without $\text{Ph}_3\text{P} = 47.7\%$	168 168
$(\text{COD})\text{Ni}(\text{1,2-diketones})\text{RCO}_2\text{NiO}_2\text{CR}$, R = C ₅ hydrocarbonyl; R ₁ = C ₁₋₃ haloalkyl, e.g., $\text{CF}_3\text{CO}_2\text{Ni}(\text{2-ethylhexanoate})/(\text{C}_2\text{H}_5)_2\text{AlCl}_2$ (31:194)	1-butene olefins C_{4-6} , e.g., hexene/ 65°C	oligomers C_{6-12} olefins $\text{C}_{12} = 97\%$	conv = 5%	160 155 206 155
$\text{Ni}(\text{octanoate})_2/(\text{C}_2\text{H}_5)_2\text{AlCl}_2$ $\text{Ni}(\text{acac})_2$ supported on $\text{SiO}_2/\text{Al}_2\text{O}_3/(\text{C}_2\text{H}_5)_2\text{Al}_2\text{Cl}_3/\text{monoolefins}$, diolefins	1-butene olefins C_{2-10} , e.g., butene/ toluene, $0-130^\circ\text{C}$, 1-100 atm	olefins C_8 (85%), C_{12} (12%), C_{16} (3%)	conv = 75% 0.11 L or product (mol of catalyst) ⁻¹ h ⁻¹	
$\text{Ni}(\text{carboxylate})$ 11% $\text{Ni}/(\text{C}_2\text{H}_5)_2\text{AlCl}_2/\text{CF}_3\text{CO}_2\text{H}$, $(\text{CF}_3\text{CO})_2\text{O}$	1-butene + 2-butene/ isohexane, 42°C , 5 bars, 4 h	olefins C_8 (89%), C_{12} (10%), C_{16} (1%)	conv = 67-98%	338 95
$\text{Ni}(\text{acac})_2$ supported on $\text{SiO}_2/\text{Al}_2\text{O}_3/(\text{C}_2\text{H}_5)_2\text{Al}_2\text{Cl}_3/\text{Ph}_3\text{P}$ or Bu_3P (1:1-20:3) $(\text{COD})_2\text{Ni}_2(\text{CO})_2$ supported on $\text{Al}_2\text{O}_3/\text{SiO}_2$ (12-87)	1-butene/isooctane, 145°F , 15 bars, 3 h 1-hexene/cyclohexane, 150°C , 1.4 h	olefins C_8 olefins C_8 (78%), C_{12} (17%), C_{24} (4%)	conv = 50%	94, 154
5% $\text{NiO}/\text{Al}_2\text{O}_3/\text{SiO}_2/(\text{C}_2\text{H}_5)_2\text{AlCl}_2$ (Al/Ni = 1)	butenes/ 50°C	olefins C_8 (50%), C_{12} (13%), C_{2-16} (37%)	1562 g of oligomer (g of Ni) ⁻¹ h ⁻¹ conv = 63%	376
$\text{Ni}/\text{Al}_2\text{O}_3/\text{AlCl}_3/(\text{C}_2\text{H}_5)_2\text{AlCl}$	60% <i>n</i> -butenes-40% butane/ 54°C , 6 h	olefins C_8 (60%), $\text{C}_{>12}$ (40%)	conv = 79%	382 162, 161


$W[O(CH_2CH_2)_nCl]_2Cl_2/(C_2H_5)_2AlCl/D$; $D = (C_2H_5)_2O, (C_2H_5)_2O, CH_3OC_2H_5$	Tungsten 2-methyl-1-pentene	olefins C_{12-24} D donor strength $\uparrow \bar{M}_w$, α	172
$WC_2/LiAlH_4$	1-hexene/25 °C, 75 min, chlorobenzene	branched-chain oligomers, $\bar{M}_w = 1230$	171
WF_3 /branched-chain aliphatic alcohols	1-butene/42 °C, 40 min	olefins C_{12-26} (10%), C_{20-24} (21%), C_{2-28} (69%)	383
Cp_2M supported on $Al_2O_3/SiO_2/(C_2H_5)_2Al_2Cl_3$, M = Cr, Fe, Co, Ni (Al/M = 0.5)	Chromium, Iron, Cobalt, Nickel butene-butane/70 °C, 30 min	olefins C_8 (80%), C_{12} (12%), C_{18} (8%), linearity = 78%	270
$C_2H_5AlCl_2/RCI$ (1:1.5-2)	Aluminum 1-hexene/293 K, 90 min heptane/hexane = 1:1	high branched-chain oligomers	177
R_nAlX_{3-n}/RCI ; X = halogen; R = H, alkyl, alkoxy; $n = 0-3$	olefins C_{3-11}	conv = 50-100% RCI activity: t -BuCl > allyl Cl > PhCl > Ph ₂ CCl	343
R_nAlX_{3-n}/R^1Cl , R = alkyl C_{1-18} , aryl C_{6-10} , R ¹ = alkyl C_{1-20} , cycloalkyl C_{6-8} , alkenyl C_{3-6} , arylalkyl C_{7-9} ; X = Cl, Br, I	1-decene/18-22 °C		179
R_nAlX_3 or $R_nAlX_{3-n}X_2$, R = hydrocarbyl; X = Br, I; $n = 1, 3$	1-decene/42 °C, 15 min, hexane	oligomers viscosity = 82.86 csT (100 °C)	385
$AlCl_3$ /alkylaluminum halide (0.7-1.5%)	α -olefins C_{6-16} /70-80 °C α -olefins C_{22} /hexane	1-decene oligomer, viscosity = 20.5 csT (100 °C)	283
R_nAl/RCI , R = hydrocarbyl	1-hexene/70 °C, 24 h, nonpolar solvent	olefins C_{12} (20%), C_{18} (40%), C_{24} (10%)	178
AlX_3 or $RAIX_2$ /haloalkanoic acid, X = Cl, F (C_2H_5) ₂ AlOC ₂ H ₄ /zeolite (10X)	isobutene/160 L (kg of catalyst) ⁻¹ h ⁻¹ , 40 °C	olefins C_8 (65%), C_{12} (25%)	386
$AlCl_3/i-C_3H_7OH$ (19:0.7)	1-dodecene/25 °C, 3 h	oligomer viscosity = 96.4 csT (37.8 °C)	182
$AlCl_3$	olefins C_{4-10} /50 °C, 1.5 h, heptane	oligomer viscosity = 77.58 csT (38 °C)	166, 388
$(C_2H_5)_2Al_2Cl_3, C_2H_5AlCl_2$	fraction $C_4H_{10}-C_4H_8/-60$ and +25 °C, heptane	$\bar{M}_w = 1000$	173
$AlCl_3/Al_{n-1}O_n/AcO(CH_2)_nOAc$, n = 2, 3, 4 $AlCl_3$ /alkyl aromatic hydrocarbons containing O and N ligands $AlCl_3$	olefins C_{6-10} /100 °C, 5 h 1-decene	oligomers viscosity = 41.7 csT (40 °C)	183
$AlCl_3/Al_2O_3$ $AlCl_3$ /alkyl aromatic hydrocarbons	1-hexene, 1-decene/103 °C, 1 h	oligomers vinylidene (53-58%), trans C=C (30-33%), trisubstituted C=C (10-16%)	389
AlH_3 /Davison SiO_2 (3.8% Al)	1-butene/-20 to +5 °C, <i>n</i> -hexane	oligomers C_3 (3%), C_{12} (81%), C_{16} (16%)	390
BF_3 /alcohols C_{4-8}	isobutene/65 °C, 1 atm	oligomers C_{20-60} (max C_{30-40})	391
BF_3/n -BuOH, $CH_3COC_2H_5$, or $HO(CH_2)_nOH$	1-decene (61% in feed- stock)/-10 and +40 °C, fixed-bed reactor 1-decene/20 psig, 49-50 °C	oligomers C_{20} (10.6%), C_{30} (58.3%), C_{40} (19.9%), C_{50} (3.9%)	184
		conv = 92.7%	187

TABLE VIII (Continued)

catalyst	olefin/react condn	products	yield	ref(s)
BF ₃ /BuOH	linear olefins: C ₉₋₁₁ , internal C ₁₃₋₁₆ /85-86 °C, 105 min	dimers (61.3%), trimers (25.1%)	conv = 87.1%	186, 409
BF ₃ /C ₂ H ₅ OH or C ₄ H ₉ OH	1-decene/10 psig, 20-25 °C, 4-6 h, continuous process	olefins C ₃₀ (59-60%), C ₄₀ (23-19%)		410
BF ₃ /SiO ₂ /H ₂ O	1-decene/29-36 °C, 12 h, 45 cm ³ /h	olefins C ₂₀ (37.8%), C ₃₀ (49%), C ₄₀ (10%)	conv = 84.4%	411, 415
BF ₃ /O ₂ /SiO ₂	1-decene/10-15 °C	olefins C ₂₀ (12-14%), C ₃₀ (53-58%), C ₄₀ (18-19%), C ₅₀ (3-6.6%)		191, 194
BF ₃ (1-20%)/Al ₂ O ₃ BF ₃ /cocatalysts	2-butene/100 psig, 150 °C 1-decene/two-step oligomerization	olefins C ₈ (81%)	conv = 51.4%	192 412
BF ₃ /CH ₃ OH BF ₃ , H ₂ O/BF ₃ (gas)	2-butene/CH ₂ Cl ₂ 1-octene/7 °C, 2 h	oligomers C ₉₋₂₀ (60%) oligomers C ₁₆ (0.6%), C ₂₄ (7.2%), C ₃₂ (92.2%)	conv = 93.4%	188 413
BF ₃ /H ₂ O or alcohols BF ₃ /mannitol (3.1:1) BF ₃ /H ₂ O, alkanolic acids	1-alkenes 1-decene 1-hexene, 1-decene, 1-tetradecene/30 °C	oligomers high branched-chain dimers to pentamers	conv = 70%	414 189 196, 418
BF ₃ (gas)/BF ₃ ·2H ₂ O	1-hexene/1-1.5 psig, 20-50 °C	olefins C ₁₂ (1.8%), C ₁₈ (68.4%), C ₂₄ (29.5%)	conv = 99%	417
BF ₃ /n-BuOH	1-butene, 1-pentene, 1-decene/50 psig, 50 °C	dimers	conv = 40%	135
BF ₃ /Al ₂ O ₃ BF ₃ /NiO, Cu ₂ O, Cr ₂ O ₃ , CoCO ₃ , or NiF ₂ , CoF ₂ BF ₃ /n-BuOH, C ₂ H ₅ COOH	butene/30 bar, 75 °C α-olefins C ₄ /C ₁₀ /C ₁₄ (4:1:1) α-olefins C ₄ /C ₆ /C ₈₋₁₈ (3.6:1:1)/23-49 °C, 1-2.5 h	oligomer C ₂₀₋₂₂ oligomers C ₈₋₃₀	conv = 32-92%	419 420 130, 421
BF ₃ /Nafion 501 BF ₃ /CH ₃ OH, C ₂ H ₅ COOH, H ₃ PO ₄ , or H ₂ O (1:1)	α-olefins C ₁₂₋₁₈ /85 °C, 2 h 3-methyl-1-butene/0-70 °C, hexane	dimers (59%), trimers (15%) dimers to hexamers	conv = 97%	422 423
BF ₃ /(CH ₃ OH/BF ₃)	1-decene/2 psig, 30 °C, 2 h, 0.2 mol of catalyst per 100 g of 1-decene	oligomers C ₃₀ (84%)		170
Ni/mordenite (Si/Al = 9)	Heterogeneous Inorganic Systems butenes (butane-butadiene)/ 16 bar, 42 °C, 0.29 mg of catalyst L ⁻¹	liquid oligomers		393
0.1-1.5% by wt Ga/ZSM-5 SiO ₂ , Al ₂ O ₃ , MgO, or TiO ₂ /H ₂ PO ₄ Cd or Zn/Al ₂ O ₃ /SiO ₂ Al ₂ O ₃ /TiO ₂ /F (Al/Ti = 90:10)	olefins C ₂₋₅ isobutene/170-293 K olefins C ₂₋₈ /30 bar, 50-500 °C isobutene in butenes/120 °C, 30 min	oligomers bp = 343 °C oligomers C ₂₀₋₆₀		394 395 396 398
WO ₃ /γ-Al ₂ O ₃ WO ₃ /Al ₂ O ₃ /F (Al/W = 100:0.5-10)	isobutene/1 atm, 150 °C isobutene/120 °C, 30 atm	oligomers C ₈ (19.5%), C ₁₂ (55.2%), C ₁₆ (20.3%) oligomers C ₁₂₋₁₆ oligomers C ₈ (18.2%), C ₁₂ (56.3%), C ₁₆ (21.4%) oligomers C ₈ (29.3%), C ₁₂ (49.2%), C ₁₆ (19.2%)	conv = 98.8%	384 399
ZrO ₂ -MoO ₃ (100:13)	isobutene/120 °C, 30 min	oils internal olefins C ₈₋₂₄	conv = 90.4%	400
K ₂ O/CaO/Fe ₂ O ₃ /Nb ₂ O ₅ /Al ₂ O ₃ /SiO ₂ MSO _n /nHCl, M = Zn, Sn, Pb, Cu, Ti, Cd, Hg; n = 0.2-1.7	olefins C ₉₋₁₄ isobutene			401 402
CuSO ₄ ·2HCl (1:2) on mineral supports 5%Cr/Al ₂ O ₃ /SiO ₂ 12.9% TaCl ₅ /SiO ₂	isobutene/0-60 °C 1-hexene 1-butene/500 psig, 150 °C	oligomers C ₁₂ oligomers C ₁₂₋₁₈ olefins C ₈ (38%), C ₁₂ (31%), C ₁₆ (19%), C ₂₀ (12%)	conv = 95%	363 403 406

Ta_2O_5/Al_2O_3 Zn/HZSM-5 zeolite	1-butene/170 °C butenes, olefins C_{4-9} /800 psig, 120–230 °C, 0.5 LHSV	olefins C_8 (7%), C_{12} (6%) for C_4 olefins C_{16} (60%), for C_{4-9} olefins C_{12-15} (max C_{12}), 1% aromatic hydrocarbon	404 440
Ni/HZSM-5 $TaCl_5/SiO_2$	butene/120–230 °C 1-hexene/100 psig, 100 °C	olefins C_{16} olefins C_{12} (69%), C_{18} (14%), $C_{>24}$ (17%)	303 406
SiO_2, Al_2O_3, TiO_2 , or ZrO_2/H_3PO_4	<i>n</i> -butene, isobutene/200 Torr, 20 °C	oligomers C_{8-12} oligomerization and meta- thesis products	395, 407
CaY zeolite Bulgarien mordenite	isobutene, <i>cis</i> -2-butene/80 °C butanes	oligomers C_{8-12} oligomerization and meta- thesis products	416 139
Wyoming bentonite (cation exchanged)	olefins C_{2-10} /85–100 °C	alkenes (80%), alkanes (3–17%), aromatic hydrocarbon (9–40%)	424
zeolite HKL	isobutene/160 °C	olefins C_8 (62.9%), C_{12} (36.5%)	196
HZSM-5/Cr(V), V(IV), or Zn(II)	isobutene/320 °C, 10^{-5} mol of isobutene (g of catalyst) $^{-1}$ s $^{-1}$	oligomers C_{8-10} (60%)	197
HZSM-5	1-hexene/359–593 K	oligomers C_{8-16} (max C_{12}) cracking, isomerization and aromatization products	342
HZSM-12	α -olefins C_6, C_8, C_{10} /200–400 psig, 392–482 °F	for C_6 olefins C_{10} (97%), for C_8 olefins (67%), C_{16} (84–88%), C_{24} (11–14%), for C_{10} olefins C_{20} (62–72%) oligomers M_w low	442
ZSM-5	olefins C_{2-6} /30–100 bar, 200–300 °C	oligomers C_{8-12} oligomers C_8 (70%), C_{12} (23%), C_{18} (7%)	425 426
L and Y zeolites: mordenite, erionite, and pentasil HM/mordenites (Si/Al = 6)	isobutene/50–200 °C 1-butene/51 bar, 473 K	highly branched oligomers reactivity: <i>trans</i> -2-butene < <i>cis</i> -2-butene < 1-butene	427 428, 335 199
Zeolon 100H (H-type mordenite) NaHY zeolite NaY zeolite/($SiO_2/Al_2O_3 = 5.22$)	isobutene/293 K butenes/293 K butenes/293 K	linear and branched olefins oligomers C_8 (92%), C_{12} (8%) oligomers C_8 (15.4%), C_{12} (5.4%)	443 271 433, 434 435, 309
HCaniy zeolite Y zeolites/Ca(II), Mg(II) $Na_2O/SiO_2/Al_2O_3$ (114:1)/ H_2O or <i>t</i> -BuOH (0.5%) SiO_2/Al_2O_3 (20–50%)	isobutene/110 °C, 100 h $^{-1}$ 1-butene isobutene/35 atm, 80 °C isobutene/1–50 atm	oligomers C_{8-12} highly branched oligomers	438 375 432
SiO_2/Al_2O_3 (15–85%)/F Cu, Zr, Al orthophosphate AlPO $_4$ /F	butenes/14 bar, 160 °C butenes 2-butene, 2-hexene/1000 psig, 300–350 °C	oligomers C_{8-12} highly branched oligomers	269
BPO $_4$	1-decene	oligomers	391 429, 430
MgCl $_2$ /KU-2-8 cation exchanger wofatite OK 80	olefins C_{4-6} isobutene	olefins C_8 (74%), C_{12} (11%), C_{16} (15%)	31
benzylsulfonic acid siloxane	isobutene/1 atm, 130 °C	olefins C_8 (52%), C_{12} (40%), C_{16} (3%)	438 380
amberlist 15 nafion 425 (perfluorosulfonic acid resin)	isobutene/7 bar, 60 °C isobutene/145 °C, 1000 h	olefins C_8 (50.8%), C_{12} (47.5%), C_{16} (1.8%) oligomers C_{28} and higher	334
nafion 501	α -olefins C_{14-20}		

TABLE VIII (Continued)

catalyst	olefin/ react condn	products	yield	ref(e)
ion exchanger/SO ₃ H	isobutene/18 atm, 48 °C	oligomers		185
H ₃ PO ₄ /C ₆₀ Lewis and proton acids	Miscellaneous isobutene 2,4,4-trimethyl-1(or 2)-pentene	oligomers C ₁₆	436 190	
(COD) ₂ Ni/PR ₃	Oligomerization of Strained Alkenes 	Alkenes dimers, trimers	447	

The mixed catalytic system TiCl₄/Ti(OBu)₄/Zr(OBu)₄/Et₃Al₂Cl₃ (1:2:1:10) oligomerizes with high yield 1-decene to a product having an average molecular weight of $M_n = 356$.⁸⁷

Octene trimers are the main products of the 1-octene oligomerization in the presence of the system TiCl₄/Et₃Al₂Cl₃.¹⁷⁰

ZrCl₄ modified with AlCl₃ oligomerizes 1-decene to trimers and tetramers with yield of 93%.¹⁶⁹

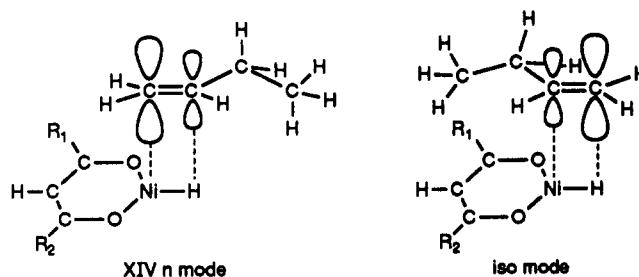
All of these titanium and zirconium catalysts have one deficiency: they promote alkylation of olefins with aromatic solvents. Zirconium catalysts are more active in this reaction, e.g. the Zr(Oi-Pr)₄/Et₃Al₂Cl₃ system alkylated toluene with 1-hexene with 100% efficiency (no 1-hexene oligomers) when the TiCl₄/Et₃Al₂Cl₃ system gave only 12% of the alkylation reaction products.¹⁶⁸

V.1.2. Nickel

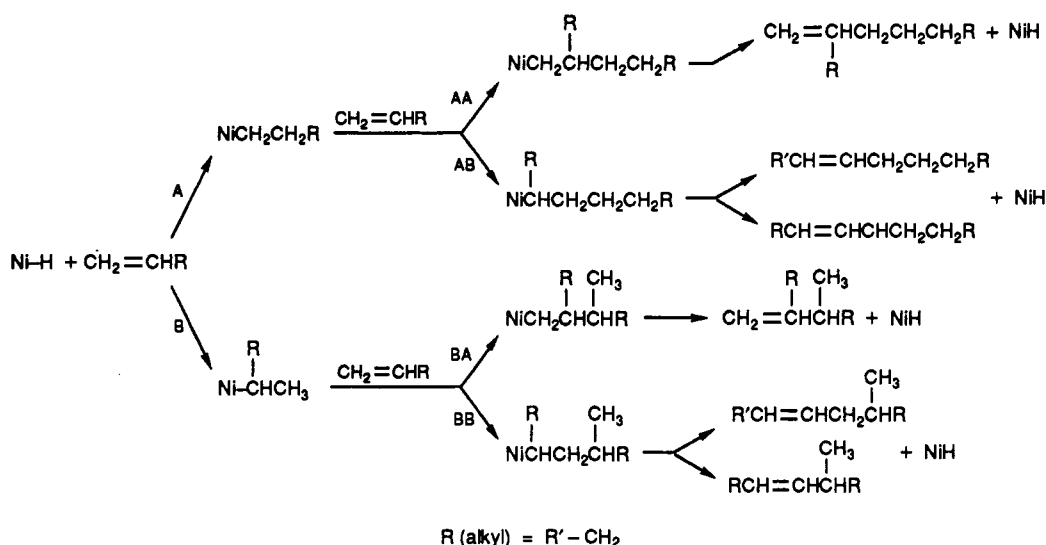
The sulfonated ylide nickel complex XVII activated with Et₂AlOEt cooligomerizes ethylene with higher olefins, e.g. 1-hexene, 1-heptene, 1-octene, and 1-decene. The mechanism of this reaction has been presented earlier (see Chapter III.1.3). Olefin insertion into the Ni-H bond is nonselective in this case (Scheme XIII, steps A and B). The chain-propagation step α -olefin insertion into the nickel-alkyl bond is also nonselective. Olefin insertion leading to the primary Ni-C bond formation (Scheme XIII, step A) is 60% more probable. Olefin reactivity in the propagation step decreases considerably together with their chain prolongation. The Ni-C bond reactivity in the olefin insertion reaction depends on the structure of an alkyl group bonded to the nickel ion. Relative reactivity in this reaction of the Ni-C bonds NiCH₂CHRCH₂R' (R = C₈H₁₇), NiCH₂CHRCH₂R' (R = C₄H₉), and NiCH₂CH₂CH₂R' equals 0.5:0.7:1.0.⁵⁸

Reactivity of the Ni-C bonds in the β -hydrogen elimination reaction depends strongly also on the alkyl group structure: β -hydrogen is eliminated at a rate 2.5 times faster from NiCH₂CHRCH₂R' group compared to the NiCH₂CH₂CH₂R' group.⁵⁸

The complex XIV A (η^3 -C₈H₁₃)Ni-(CH₃COCHCOCH₃), XIV B (η^3 -C₈H₁₃)Ni-(CF₃COCHCOCH₃), and XIV C (η^3 -C₈H₁₃)Ni-(CF₃COCHCOCF₃)—see Chapter III.1.3.— are very active in the 1-butene oligomerization.^{53,55,160} Two 1-butene orientations: "n mode" and "iso mode" are possible during its insertion to the Ni-H bond.



Reduction in electron density in the nickel ions in the complexes XIV A,B,C caused by an increase of the number of fluorine atoms in the acetylacetonate moiety, increase the catalytic activity of these complexes and the stability of the n-mode intermediate in the following

SCHEME XIII. High α -Olefin Oligomerization Mechanism in the Presence of a Nickel Complex Catalyst^{53,54}

^a (A) Addition of the olefin primary carbon to the nickel atom. (B) Addition of the olefin secondary carbon to the nickel atom.

order: XIV C > XIV B > XIV A and favors the occurrence of reaction A Scheme XIII.^{53,54} The insertion of 1-butene into the Ni-H bond occurs mainly according to the Markovnikov rule—*n* mode (90%). Insertion of the next 1-butene molecule into the penultimate nickel-alkyl bond occurs with only 12% Markovnikov selectivity. This indicates that steric effects are more important than electronic influences in 1-butene oligomerization in presence of the complexes XIV.⁵⁵ Various solvents have been tested in this reaction and the following increasing order of effectiveness has been established: toluene > fluorobenzene > *n*-heptane. Polar solvents block the catalyst active centers; acetonitrile and DMF destroy these nickel complexes.⁵³

The system Ni(acac)₂/Et₃Al₂Cl₃ is active in 1-hexene oligomerization. Its modification with donor ligands, e.g. PPh₃, increases the yield and molecular weight of obtained products, mainly trimers.¹⁶⁸ Similar systems with trifluoroacetylacetonate ligands and with PPh₃¹⁵³ or PBu₃¹⁵⁴ phosphines and the system RCOONiOOCR'/EtAlCl₂ where R = CF₃, R' = 2-ethylhexanoate^{155,156} gave dimers and trimers in 1-butene oligomerization.

In presence of sulfur ligand containing systems, Ni(*p*-toluensulfonato)₂/EtAlCl₂¹⁵⁷ and Ni(pentene-2,5-dithionato)/P(R¹R²R³)X (R = alkyl or aryl, X = halogen), only butene dimers have been obtained.¹⁵⁸

Heterogenized catalysts have also been tested in this reaction. Calcinated nickel salts supported on alumina and activated with (*sec*-BuO)₃Al or a AlCl₃ + Et₂AlCl mixture^{159,161,162} oligomerized butenes to C₈₋₁₂ olefins. Similar results have been obtained in the presence of the system Cp₂Ni/Al₂O₃-SiO₂/Et₃Al₂Cl₃.²⁷⁰

V.1.3. Tungsten

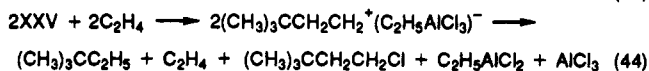
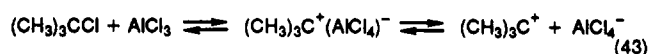
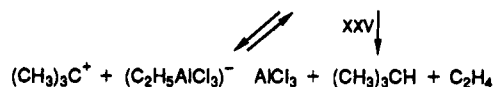
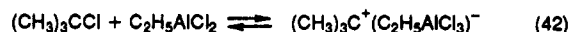
WCl₆/LiAlH₄¹⁷¹ and W[OCH(CH₂Cl)₂]₂Cl₄/Et₂AlCl/ether (ether = Bu₂O, Et₂O, MeOPh)¹⁷² catalytic systems oligomerize 2-methyl-1-pentene and 1-hexene.

V.1.4. Aluminum

Chloroalkylaluminum compounds are described as active catalysts for various olefin oligomerizations. The

mixed system Et₃Al₂Cl₃/EtAlCl₂ was used for oligomerization of butenes.¹⁷³ 1-Hexene dimers, trimers, and tetramers are obtained in the presence of the following systems: EtAlCl₂/Cl₃CCOOH and EtAlCl₂/CF₃SO₃H, which can be called superacids.¹⁷⁴⁻¹⁷⁶

Cationic mechanism of the 1-hexene oligomerization for the EtAlCl₂/RCl (R = alkyl or aryl) catalyst was established as follows:¹⁷⁷



In the system EtAlCl₂/RCl the catalyst efficiency decreases in the following order: (CH₃)₃CCl > CH₂=CHCH₂Cl > C₆H₅Cl > (C₆H₅)₃CCl.¹⁷⁷ The products obtained with this catalytic system are branched. The same mechanism was proposed also for the 1-decene oligomerization.

V.2. Lewis and Brønsted Acids as Catalysts

AlCl₃ and BF₃ are catalysts for higher α -olefins' oligomerization.¹⁸⁰ For their action, they need the presence of labile proton cocatalysts in many cases. 1-Butene is oligomerized in presence of AlCl₃ modified with *n*-butylbenzene or xylenes.¹⁸¹ An increase in catalyst concentration increases the reaction yield up to 100% when the catalyst concentration reaches 1.5% by weight. An increase in the reaction temperature causes a decrease in the oligomer molecular weight.

The system AlCl₃/tertiary or quaternary alcohols are described as 1-dodecene oligomerization catalysts.¹⁸²

Another catalytic system AlCl₃/poly alcohol esters are successfully used in higher α -olefins oligomerization.¹⁸³ A change from AlCl₃ in these systems to BF₃ gives active oligomerization catalysts for 1-decene,^{184,189} olefins C₄₋₁₀,¹⁸⁰ butenes,¹⁸⁶ olefins C₆₋₁₂,¹⁸⁷ and 2-butenes.^{129,188} The mechanism of all of those reactions has a cationic

character as shown in Schemes X and XI.

1-Hexene, 1-decene, and 1-tetradecene are oligomerized to highly branched di-, tri-, tetra-, and pentamers in the presence of the system $\text{BF}_3/\text{alkanoic acids}$.¹⁹⁵

The heterogeneous systems BF_3/SiO_2 and $\text{BF}_3/\text{Al}_2\text{O}_3$ were used in the 1-decene^{191,193,194} and olefins C_{4-6} ¹⁹² oligomerization.

V.3. Inorganic Oxides

Alumina-silica gels modified or unmodified with various metal ions are the most popular catalysts for higher α -olefins oligomerization.^{395,396,401,403}

The zeolite HKL ($\text{SiO}_2\text{-Al}_2\text{O}_3 = 5.2$), partly deca-tionized, is active in this reaction. Its activity depends on the amount of catalyst, not on the strength of acidic sites (Lewis and Brønsted).¹⁹⁶ These sites are mainly located on amorphous alumina-silica gel surface and macropores and in the zeolite channels and chamber walls. At temperatures higher than 573 K, besides oligomerization the olefin also undergoes cracking and aromatization reactions. Also the reaction products also take part in these reactions. The yield of aromatic products increases with temperature increase.

In the case of the H-ZSM-5 zeolite, modification with Cr(III), Cr(V), and Cr(IV) and Zn(II) ions decreases the OH groups (Brønsted acid center) concentration on the zeolite surface and on the channel walls. This results decrease in catalyst's activity in oligomerization of olefins because the reaction mainly occurs in the channels.¹⁹⁷

Investigations of butene oligomerization in the presence of a zeolite ($\text{SiO}_2\text{-Al}_2\text{O}_3 = 60.3$) modified with various metal oxides allowed the establishment of the influence of oxides on this reaction.¹⁹⁸ SiO_2 and WO_3 localize on the zeolite crystal surfaces and practically do not change the reaction selectivity. Oxides like SnO_2 , Cr_2O_3 , and Bi_2O_3 localize on the channel walls and in this way block the Brønsted acid sites. This results in an increase of aromatic product yield. Addition of ZnO favors olefin dehydrogenation. The product of this reaction becomes the intermediates for subsequent aromatization reactions. The selectivity of oligomers in this case is very low.

For the NaHY zeolite, as a catalyst, the following reactivity of butenes in the cationic oligomerization reaction was established: 1-butene > cis-2-butene > trans-2-butene.¹⁹⁹

Generally, all catalysts of this group have very low selectivity in the higher α -olefin oligomerization. Their activity, selectivity, and oligomerization reaction conditions are listed in Table VIII.

VI. Conclusions

The olefin reactivity in the oligomerization reaction decreases in proportion to the increase of the olefin length (ethylene > propylene > 1-butene > 1-hexene > 1-octene > 1-decene) and the C=C bond position (1-butene > 2-butene).

Only linear ethylene oligomers with 99% yields are obtained. In the case of higher olefin oligomerization mainly branched oligomers are the products.

Oligomerization catalysts can be divided into three groups: homogeneous and heterogeneous transition-metal complexes, trialkylaluminum compounds, and

heterogeneous and homogeneous Lewis and Brønsted acids.

The Ti(IV), Zr(IV), and particularly Ni(II), Ni(I) complexes exhibit the highest activity and selectivity in the olefin oligomerization. Their activity and selectivity depend on electronic and steric factors of the central metal ion in these complexes.

An increase in positive charge on the central metal ion caused by acceptor ligands generally increases the catalyst's activity but decreases molecular weights of the obtained oligomers.

Donor ligands make olefin insertion into the metal-carbon bond much easier. This results in an increase of the oligomer length and linearity.

Large, bulky ligands favor the formation of intermediates from which the β -hydrogen elimination becomes more difficult and therefore the higher oligomers are obtained. The presence of these ligands in these complexes contributes to a relatively high linearity of the products.

Nickel complexes, particularly ylides, are most selective and active in the ethylene oligomerization to higher linear α -olefins. They have been recently applied industrially in the SHOP process.

There are many papers concerning titanium and zirconium complexes which are also very active and selective as catalysts of olefin oligomerization. Their main deficiency is polyethylene and branched oligomers formation as side products.

The systems consisting of other metal complexes, e.g. lanthanides, are less active or are being investigated at the moment.

Cationic catalysts homogeneous and heterogeneous (e.g. AlCl_3 , metal oxides, zeolites, inorganic acids) are generally used for oligomerization of olefins possessing three or more carbons in the chain. These catalysts are less selective than transition-metal complex catalysts. In their presence, mainly high branched oligomers and products of the alkylation, cracking, aromatization, and isomerization reactions are obtained, particularly at higher temperatures.

Oligomers with high linearity are the products of the ethylene oligomerization using trialkylaluminum compounds as catalysts. Halogenoalkylaluminum compounds and the systems organoaluminum/halogeno-hydrocarbons are the catalysts of higher olefin oligomerization according to a cationic mechanism.

VII. References

- (1) Masters, C. In *Gomogenyj kataliz perehodnymi metalami*; Mir: Moscow, 1983; p 146.
- (2) Henrici-Olivé, G.; Olivé, S. In *Coordination and Catalysis*. Verlag Chemie: Weinheim, 1977; p 146.
- (3) Jolly, P. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, Stone, Abel, Eds.; Pergamon: Oxford, 1982; Vol. 8, pp 615, 649, 671. Keim, W., Behr, A., Röper, M. In *Organometallic Chemistry*; Oxford: Pergamon, 1982; Vol. 8, p 371. O'Connor, C. T.; Kojima, M. *Catal. Today* 1990, 6, 329. James, B. D.; Dain, C. J. *J. Synth. Lubr.* 1988, 5, 187. Chauvin, Y. *Ind. Appl. Homogeneous Catal.*; Mortreux, A., Francis, F., Eds.; Reidel: Dordrecht, The Netherlands, 1988; p 177. Lehmkuhl, H. *Pure Appl. Chem.* 1986, 58, 495. Onsager, O. T.; Johansen, J. E. *Chem. Met.-Carbon Bond*; Hartley, F. R.; Patai, S.; Wiley: Chichester, UK, 1985; Vol. 3, p 205; *Chem. Abstr.* 1985, 103, 214789h. Kaim, W. *Ann. N.Y. Acad. Sci.* 1983, 415, 191. Cross, R. J. *Catalysis (London)* 1982, 5, 366. Pearce, R. *Catal. Chem. Processes*; Pearce, R., Patterson, W. R., Eds.; Wiley: New York, NY, 1981; p 194.
- (4) Patat, F.; Sinn, H. *Angew. Chem.* 1958, 70, 496.
- (5) Pino, P. *Adv. Polym. Sci.* 1965, 4, 394.

- (6) Cossee, P. *J. Catal.* 1964, 3, 80. Arlman, E. J. *J. Catal.* 1964, 3, 89. Arlman, E. J.; Cossee, P. *J. Catal.* 1964, 3, 99.
- (7) Henrici-Olivé, G.; Olivé, S. *Angew. Chem.* 1967, 79, 764.
- (8) Armstrong, D. R.; Perkins, P. G.; Stewart, J. J. *J. Chem. Soc. Dalton Trans.* 1972, 1972.
- (9) Pino, P.; Consiglio, G.; Ringger, J. *Justus Liebigs Ann. Chem.* 1977, 509.
- (10) Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L.; Mahlab, R. *J. Chem. Soc., Chem. Commun.* 1978, 604. Green, M. L. *Pure Appl. Chem.* 1978, 50, 27.
- (11) Rodriguez, L. A.; van Looy, H. M.; Gabant, J. A. *J. Polym. Sci. (Part A1)* 1966, 4, 1905; 1917; 1927; 1951; 1971.
- (12) Novaro, O.; Chow, S.; Magnaut, P. *J. Catal.* 1976, 41, 91.
- (13) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* 1983, 250, 395.
- (14) Brookhart, M.; Green, M. L. H.; Pardy, R. B. A. *J. Chem. Soc., Chem. Commun.* 1983, 691; 1982, 1410.
- (15) Jolly, C. A.; Marynick, D. S. *J. Am. Chem. Soc.* 1989, 111, 7968.
- (16) Minsker, K. S.; Karpasas, M. M.; Zaikov, G. E. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* 1987, C27 (1), 1.
- (17) Langer, A. W. *J. Macromol. Sci. Chem.* 1970, 4, 775.
- (18) Bestian, H.; Clauss, K. *Angew. Chem.* 1962, 74, 955; 1963, 75, 1068.
- (19) Russiyan, L. N.; Matkovskiy, P.; Dyachkovskiy, F. S.; Brikenshtein, H. M. A.; Gerasina, M. P. *Vysokomol. Soedin. Ser. A* 1977, 19, 619.
- (20) Dyachkovskiy, F. S.; Matkovskiy, P. E.; Russiyan, L. N.; Semenov, A. A. *Vysokomol. Soedin. Ser. A* 1978, 20, 746.
- (21) Zubanov, B. A.; Zavorohin, M. D. In *Koordinatsiya i kataliz polimerizatsii olefinov*; Nauka: Moscow, 1987; pp 120-134.
- (22) Henrici-Olivé, G.; Olivé, S. *J. Polym. Sci., Polym. Lett. Ed.* 1974, 12, 39; *Adv. Polym. Sci.* 1974, 15, 1; *Polym. Prep. Am. Chem. Soc., Div. Polym. Chem.* 1974, 15, 368; *Fortschr. Hochpolym. Forsch.* 1974, 15, 1.
- (23) Russiyan, L. N.; Matkovskiy, P. E.; Dyachkovskiy, F. S.; Brikenshtein, H. M. A.; Starcheva, G. P.; Gerasina, M. P. *Vysokomol. Soedin. Ser. A* 1979, 21, 1891.
- (24) Melnikov, V. N.; Sycheva, D. A.; Matkovskiy, P. E.; Golubiev, W. K.; Chekryi, P. S. *Khim. Promst. (Moscow)* 1985, 7, 389.
- (25) Semenov, A. A.; Matkovskiy, P. E.; Dyachkovskiy, F. S. *Vysokomol. Soedin. Ser. A* 1979, 21, 2749. Matkovskiy, P. E.; Chernaya, L. I.; Russiyan, L. N. *Izv. AN SSSR Ser. Khim.* 1984, 643.
- (26) Matkovskiy, P. E.; Belova, V. N.; Brikenshtein, H. M. A.; Dyachkovskiy, F. S.; Denisova, Z. A.; Kissin, Yu. V. *Vysokomol. Soedin. Ser. A* 1975, 17, 252.
- (27) Golubev, V. K.; Melnikov, V. N.; Busheva, Z. G.; Ustinova, T. A.; Menyailo, A. T. *Khim. Promst. (Moscow)* 1979, 3, 141.
- (28) Henrici-Olivé, G.; Olivé, S. *Chem. Ing. Tech.* 1971, 43, 906.
- (29) Langer, A. W. U.S. Patent 4 396 788, 1983; 4 434 312, 1984; *Chem. Abstr.* 1984, 100, 210636w.
- (30) Aliev, V. S.; Aliev, A. B. USSR Patent 1 154 258, 1985; *Chem. Abstr.* 1985, 103, 215952t.
- (31) Popov, W. G.; Wasylichenko, S. W. *Kinet. Kat.* 1988, 29, 981.
- (32) Kolocej, I. N.; Popov, W. G.; Dawydowa, S. L.; Kabanov, W. A. *Vysokomol. Soedin. Ser. B* 1981, 23, 368.
- (33) Fuhrmann, H.; Semikolenov, V. A.; Yarmakov, Y. *React. Kinet. Catal. Lett.* 1979, 11, 301.
- (34) Fuhrmann, H.; Mix, H.; Wilcke, F. W.; Reihsig, J. German Patent 124 623, 1977; *Chem. Abstr.* 1979, 88, 7666z.
- (35) Fuhrmann, H.; Mix, H.; Wilcke, F. W.; Reihsig, J. German Patent 124 047, 1977; *Chem. Abstr.* 1978, 88, 51382f.
- (36) Longi, P.; Greco, F.; Rossi, U. *Chim. Ind. (Milan)* 1973, 55, 252.
- (37) Attridge, C. J.; Jackson, R.; Maddock, S. J.; Thompson, D. T. *J. Chem. Soc., Chem. Commun.* 1973, 4, 132.
- (38) Belova, W. N.; Matkovskiy, P. E.; Gerasina, M. P.; Brikenshtein, H. M. A.; Dyachkovskiy, F. S. In *Kompleksnyie metaloorgan cheskie katalizatory polimerizatsii olefinov*; Nauka: Moscow, 1980; p 30.
- (39) Burinina, N. A.; Piechatnikov, E. L.; Brikenshtein, H. M. A.; Gerasina, M. P.; Mel'nikov, W. N. *Zh. Prikl. Khim.* 1986, 59, 364.
- (40) Mel'nikov, V. N.; Matkovskiy, P. E.; Russiyan, L. N.; Bucheva, Z. G. *Kinet. Kat.* 1988, 29, 124.
- (41) Mel'nikov, V. N.; Matkovskiy, P. E.; Sycheva, O. A.; Chernyh, S. P.; Chekryi, P. S.; Belova, W. N.; Russiyan, L. N.; Gerasina, M. P. *Khim. Promst. (Moscow)* 1986, 5, 261.
- (42) Mel'nikov, V. N.; Sycheva, O. A.; Matkovskiy, P. E.; Moreva, T. A.; Chernyh, S. P.; Chekryi, P. S.; Belova, W. N.; Russiyan, L. N. *Khim. Promst. (Moscow)* 1986, 6, 823.
- (43) Langer, A. W. U.S. Patent 4 442 309, 1984; *Chem. Abstr.* 1987, 66, 19045c.
- (44) Langer, A. W.; Steger, J. J.; Burkhardt, T. J. U.S. Patent 4 361 714, 1982; *Chem. Abstr.* 1983, 98, 35150z.
- (45) Kuliev, R. Sh.; Akhmedov, V. M.; Gasanova, R. Z. *Neftepererab. Neftekhim.* 1985, 4, 15.
- (46) Kuliev, R. Sh.; Akhmedov, V. M.; Khanmetov, A. A.; Gasanova, R. Z.; Pivmedov, G. *Neftepererab. Neftekhim.* 1986, 6, 14.
- (47) Pino, P.; Lorenzi, G. P. In *Preparation and Properties of Stereoregular Polymers*; D. Reidel: Holland, 1980; p 21.
- (48) He, R.; Jiang, J.; Wang, Y.; Zhou, K. *Cuihua Xuebao* 1988, 9, 58; *Chem. Abstr.* 1988, 109, 55309.
- (49) He, R.; Jiang, J.; Wang, Y.; Zhou, K. *Fenzi Cuihua* 1988, 2, 283; *Chem. Abstr.* 1989, 110, 232136a.
- (50) Langer, A. W. U.S. Patent 4 377 720, 1983; *Chem. Abstr.* 1983, 98, 198893h.
- (51) Bogdanovic, B.; Henc, B.; Karmann, H. H. *Ind. Eng. Chem.* 1970, 62, 35.
- (52) Muzzio, F. J.; Löffler, D. G. *Acta Chim. Hung.* 1987, 124, 403.
- (53) Keim, W.; Hoffmann, E.; Lodewick, R.; Pauckert, M.; Schmitt, G.; Fleischhauer, J.; Meier, U. *J. Mol. Catal.* 1979, 6, 79.
- (54) Bogdenowic, B. *Adv. Organometal. Chem.* 1979, 17, 105.
- (55) Peuckert, M.; Keim, W.; Storp, S.; Weber, R. S. *J. Mol. Catal.* 1983, 20, 115.
- (56) Keim, W.; Behr, A.; Limbaecker, B.; Krüger, C. *Angew. Chem.* 1983, 95, 505.
- (57) Kissin, Y. V.; Beach, D. L. *J. Polym. Sci. Part A, Polym. Chem.* 1989, 27, 147.
- (58) Kissin, Y. V. *J. Polym. Sci. Part A, Polym. Chem.* 1989, 27, 605; 623.
- (59) Keim, W. *Chem. Ing. Tech.* 1984, 56, 850.
- (60) Peuckert, M.; Keim, W. *J. Mol. Catal.* 1984, 22, 289.
- (61) Matkovskiy, P.; Russiyan, L. N.; Dyachkovskiy, F. S.; Khvostyk, G. M.; Dzhabieva, Z. M.; Startseva, G. P. *Vysokomol. Soedin., Ser. A* 1976, 18, 840.
- (62) Braca, G.; Sbrana, G. *Chim. Ind. (Milan)* 1974, 56, 110.
- (63) Nefedov, B. K.; Sergeeva, N. S.; Eidus, Ya. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1974, 10, 2372.
- (64) Fernald, M. B.; Hay, R. G.; Kresge, A. N. Gulf Research, U.S. Patent 3 510 539, 1970; *Chem. Abstr.* 1970, 73, 76638 (Brit. 1 186 610, 1970).
- (65) Gruening, H.; Luff, G. *Angew. Makromol. Chem.* 1986, 142, 161.
- (66) Fernald, H. B. U.S. Patent 3 444 263, 1969; *Chem. Abstr.* 1969, 71, 60658w.
- (67) Fernald, H. B. U.S. Patent 3 478 124, 1970; *Chem. Abstr.* 1970, 72, 54711n.
- (68) Comp. Fr. Raffinage, Netherlands Patent 6 400 403, 1964; *Chem. Abstr.* 1965, 62, 2706c.
- (69) Aliev, V. S.; Mirzoeva, Z. S.; Soldatova, V. A. *Sb. Tr. Int. Neftekhim. Protsev. AN AzSSR* 1986, 15, 89.
- (70) Novakova, J.; Kubelkova, L.; Dolejssek, Z.; Jiru, P. *Collect. Czech. Chem. Commun.* 1979, 44, 3341.
- (71) Van den Berg, J. P.; Wolthuisen, J. P.; Clague, A. D.; Hays, G. R.; Huis, R.; Van Hooff, I. H. C. *J. Catal.* 1983, 80, 130.
- (72) Van den Berg, J. P.; Wolthuisen, J. P.; Van Hooff, I. H. C. *J. Catal.* 1983, 80, 139.
- (73) Mravec, D.; Balko, J.; Ilavsky, J. *Chem. Prum.* 1986, 36, 82.
- (74) Kustov, L. M.; Borovkov, V. Yu.; Kazanskyi, V. B. *Stud. Surf. Sci. Catal.* 1984, 18, 241.
- (75) Eiev, I. V.; Shelimov, B. N.; Kazanskyi, V. B. *Kinet. Katal.* 1984, 25, 1124.
- (76) Lapidus, A. L.; Slinkin, A. A.; Rudakova, L. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1974, 9, 1956.
- (77) Turner, A. H. *J. Am. Oil Chem. Soc.* 1983, 60, 623.
- (78) Lanier, C. U.S. Patent 3 789 081, 1974; *Chem. Abstr.* 1972, 76, 26950d.
- (79) Gulf Research Co. British Patent 1 186 610, 1970; *Chem. Abstr.* 1970, 73, 76638s; 1 186 609, 1970; *Chem. Abstr.* 1970, 73, 56608c; U.S. Patent 3 655 809, 1972; *Chem. Abstr.* 1972, 77, 4836q; 3 721 719, 1973; *Chem. Abstr.* 1972, 77, 4849u; 3 751 618, 1973; *Chem. Abstr.* 1973, 79, 91550z.
- (80) Keim, W. *Stud. Surf. Sci. Catal.* 1986, 25, 201. Lutz, E. F. *J. Chem. Educ.* 1986, 63, 203. Behr, A.; Keim, W. *Arabian J. Sci. Eng.* 1985, 10, 377. Keim, W. *New J. Chem.* 1987, 11, 531. Freitas, E. F.; Gum, C. R. *Chem. Eng. Prog.* 1979, January, 73.
- (81) Nieuwenhuis, R. A. *Petrol. Techn.* 1980, 268, 46. Spitzer, T. M. *Seifen, Oele, Fette, Wachse* 1981, 107, 141.
- (82) Reuben, B.; Wittcoff, H. *J. Chem. Educ.* 1988, 65, 605.
- (83) Melnikov, V. M.; Matkovskiy, P. F.; Sycheva, O. A.; Zavorotof, V. I.; Chekry, P. S. USSR Patent SU 1 211 249, 1986; *Chem. Abstr.* 1987, 107, 97342b.
- (84) Rischina, L.; Zhuravleva, E. N.; Kissin, Yu. V.; Pitrogov, O. N.; Chirkov, N. M. *Vysokomol. Soedin. Ser. A* 1974, 16, 1459.
- (85) Motier, J. F.; Yoo, J. S. U.S. Patent 3 855 341, 1974; *Chem. Abstr.* 1975, 83, 115539c.
- (86) Watanabe, M.; Kuramoto, M. Eur. Pat. Appl. EP 268 214, 1988; *Chem. Abstr.* 1988, 109, 21161.
- (87) White, M. A. Ger. Offen. DE 3 500 638, 1985; *Chem. Abstr.* 1986, 104, 6843n; U.S. Patent 4 579 991, 1986; *Chem. Abstr.* 1986, 104, 6843n.
- (88) Yang, Z.; Zhao, Y. *Shiyou Huangong* 1986, 15, 343; *Chem. Abstr.* 1986, 105, 153596k.
- (89) Pruvot, A.; Commereuce, D.; Chauvin, Y. *J. Mol. Catal.* 1983, 22, 179.
- (90) Gao, Z.; Wang, G.; Zhou, K. *Cuihua Xuebao* 1985, 6, 390; *Chem. Abstr.* 1986, 104, 16793k.
- (91) Gao, Z.; Lin, Z.; Wang, H.; Zhou, K. *Gaodeng Xuexiao Hua-*

- tue Xuebao 1985, 6, 1127; *Chem. Abstr.* 1986, 104, 207783d.
- (92) Yoo, Y. S.; Milam, R. L. U.S. Patent 3 697 617, 1972; *Chem. Abstr.* 1973, 78, 3652.
- (93) Yoo, Y. S.; Erickson, H. U.S. Patent 3 992 323, 1976; *Chem. Abstr.* 1977, 86, 73408.
- (94) Atlantic Richfield Co. Japanese Patent 7 509 592, 1975; *Chem. Abstr.* 1976, 84, 106354.
- (95) Cannell, L. U.S. Patent 3 592 869, 1971; *Chem. Abstr.* 1971, 75, 98144v.
- (96) Skupiński, W.; Malinowski, S. *J. Organometal. Chem.* 1975, 99, 465.
- (97) Malinowski, S.; Skupiński, W. *Ann. Soc. Chim. Pol.* 1974, 48, 359.
- (98) Skupiński, W.; Malinowski, S. *J. Mol. Catal.* 1978, 4, 95.
- (99) Skupiński, W.; Malinowski, S. *J. Organometal. Chem.* 1976, 117, 183.
- (100) Watson, P. L. *J. Am. Chem. Soc.* 1982, 104, 337.
- (101) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* 1985, 107, 3091.
- (102) Jesko, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* 1985, 107, 8103.
- (103) Andreas, F.; Grobe, K. In *Propylenchemie* (Polish translation); *Chemia propylenu*; WNT: Warszawa, 1974; p 310.
- (104) Repas, M. *Chem. Tech.* 1965, 17, 222; *Chem. Prum.* 1965, 15, 543.
- (105) Chkheidze, O. Y.; Potolovskiy, L. A.; Doladugin, A. I. *Tr. Vses. Nauchno-Issled. Inst. Pererab. Nefti* 1963, 9, 228; *Chem. Abstr.* 1963, 60, 1568.
- (106) Chkheidze, O. Y.; Akiszina, L. A.; Burova, L. M. *Neftepi-erab. Neftekhim.* 1966, 28.
- (107) Piechaczek, F.; Fabisz, E.; Burczyk, R. Polish Patent 57 962, 1969; *Chem. Abstr.* 1970, 72, 48064.
- (108) Muchinsky, D. Y. *Izvest. Akad. Nauk Turkmen. SSR* 1960, 6, 58; *Chem. Abstr.* 1961, 55, 15 902.
- (109) Fabisz, E.; Cwik, R.; Musiol, R.; Pilarczyk, H. Polish Patent 104 719, 1982; *Chem. Abstr.* 1982, 95, 61451.
- (110) Galimov, Z. F.; Rakhimov, M. N.; Belayeva, E. G.; Vinyukova, N. I. *Neftepi-erab. Neftekhim.* 1985, 18.
- (111) Morrell, J. C. U.S. Patent 2 586 852, 1952, (see ref 103).
- (112) Shell Dev. Co. U.S. Patent 2 619 512, 1952, (see ref 103).
- (113) British Patent 969 403-4, 1964, (see ref 103).
- (114) Ipatieff, V. N. *Ind. Eng. Chem.* 27, 1067, 1935, (see ref 103).
- (115) Calif. Res. Corp. U.S. Patent 2 852 579, 1958, (see ref 103).
- (116) German Patent, 885 701, 1948, (see ref 103).
- (117) British Patent 710 537, 1954, (see ref 103).
- (118) Bielawski, M. S.; Mavity, J. M. U.S. Patent 2 618 614, 1952, (see ref 103).
- (119) Marsh, S. K.; Owen, H.; Wright, B. S. Eur. Pat. Appl. 0 126 527, 1987; *Chem. Abstr.* 1984, 101, 113725n.
- (120) Marsh, S. K.; Owen, H.; Wright, B. S. Eur. Pat. Appl. 0 127 283, 1987; *Chem. Abstr.* 1984, 101, 75742f.
- (121) Corner, E. S.; Lynch, C. S. U.S. Patent 2 778 804, 1957, (see ref 103).
- (122) Mavity, J. M.; Bielawski, M. S. U.S. Patent 2 692 241, 1954 (see ref 103).
- (123) U.S. Patent 2 537 282, 1946, (see ref 103).
- (124) Kemp, J. D. U.S. Patent 2 826 622, 1958 (see ref 103).
- (125) Topcheyv, A. V.; Pushkin, J. *Dokl. Akad. Nauk SSSR* 1947, 58, 1057.
- (126) British Patent 727 944, 1955, (see ref 103).
- (127) Muessig, C. W.; Lippincott, S. B. U.S. Patent 2 816 944, 1957, (see ref 103).
- (128) Yoneda, N.; Yoshida, H.; Ohtsuka, H. *Asahi Garasu Kogyo Gijutsu Shoreikai Kenkyu Hokoku* 1973, 22, 258; *Chem. Abstr.* 1975, 83, 59408.
- (129) Lachance, P.; Eastham, A. M. *J. Polym. Sci., Polym. Symp.* 1976, 203.
- (130) Larkin, J. M.; Watts, L. W. U.S. Patent 4 417 082, 1983; *Chem. Abstr.* 1984, 100, 36916a.
- (131) Terres, E.; Ebert, R.; Loebmann, K. H.; Rauth, G.; Seekirch-hern, R.; Wulf, C. *Erdol Kohle* 1959, 12, 547, (see ref 103).
- (132) Petrow, A. *Fette-Seifen Anstrichmittel* 1955, 57, 798 (see ref 103).
- (133) Anszus, L. J.; Pietrow, A. D. *Dokl. Akad. Nauk SSSR* 1950, 70, 425.
- (134) Brandes, O. L.; Gruse, W. A.; Lowy, A. *Ind. Eng. Chem.* 1936, 28, 554.
- (135) Onopchenko, A.; Cupples, B. L.; Kresge, A. N. *Ind. Eng. Chem. Prod. Res. Dev.* 1983, 22, 182.
- (136) Audisio, G.; Priola, A. *Makromol. Chem.* 1988, 189, 111.
- (137) Kubelkova, L.; Novakova, J.; Dolejssek, Z.; Jiru, P. *Collect. Czech. Chem. Commun.* 1980, 45, 3101.
- (138) Galya, L. G.; Ocellli, M. L.; Hsu, J. T.; Young, D. C. *J. Mol. Catal.* 1985, 32, 391.
- (139) Dimitrov, K.; Dimitrova, R. *God. Sofii. Univ. "Khim. Fak. Khim. Fac.* 1979, 73, 125; *Chem. Abstr.* 1984, 101, 24019.
- (140) Matreev, G. A.; Mirianashvili, V. M.; Mirzoev, T. M.; Kost-rih, L. P. *Monomyer Poluprod. Neftekhim. Sint.* 1983, 36; *Chem. Abstr.* 1985, 102, 46293.
- (141) Garwood, E. W. *ACS Symp. Ser.* 1983, No. 218 (Intrazeolite Chem), 383; *Chem. Abstr.* 1983, 99, 139251.
- (142) Quann, R. J.; Green, L. A.; Tabak, S. A.; Krambeck, F. J. *Ind. Eng. Chem. Res.* 1988, 27, 565.
- (143) Wilshier, K. G.; Smart, P.; Vester, R.; Mole, T.; Behrsing, T. *Appl. Catal.* 1987, 31, 339.
- (144) Dzwigaj, S.; Haber, J.; Romotowski, T. *Zeolites* 1984, 4, 147.
- (145) Kiricsi, I. *Magy. Kem. Lapja* 1977, 32, 605; *Chem. Abstr.* 1978, 89, 41882.
- (146) Engelhardt, J.; Kallo, D. *Acta Chim. Hung.* 1985, 119, 249.
- (147) Engelhardt, J.; Detrekoy, E.; Kallo, D. *Ropa Uhlie* 1980, 22, 609.
- (148) Espinoza, R. L.; Scurrall, M. S.; Van Walsem, H. J. *Actas Simp. Iberoam. Catal.* 1984, 2, No. 9, 1625.
- (149) Kuznetsov, O. T.; Panchenkov, G. M.; Tolkscheva, I. E. *Neftekhimija* 1980, 20, 200.
- (150) Eidus, Y. T.; Lapidus, A. L.; Rudakova, L. N. *Izw. Akad. Nauk SSSR, Ser. Khim.* 1974, 179.
- (151) Panchenkov, G. M.; Kuznetsov, A. I.; Shaiki, M. K. *Neftekhimija* 1971, 11, 18.
- (152) Dessau, R. M. Eur. Pat. Appl. EP 37 671, 1981; *Chem. Abstr.* 1982, 96, 85033f.
- (153) Gao, Z.; Zhang, A.; Liu, B.; Zhou, K. *Dalian Gongxueyuan Xuebao* 1987, 26, 32; *Chem. Abstr.* 1987, 107, 237361.
- (154) Yoo, J. S.; Erickson, H. British Patent 1 411 692, 1973; *Chem. Abstr.* 1976, 84, 60247.
- (155) Japanese Kokai 82 50 936, 1982; *Chem. Abstr.* 1982, 97, 92986. Le Penec U.S. Patent 4 398 049, 1983; *Chem. Abstr.* 1981, 95, 11476.
- (156) Chauvin, Y.; Commereuc, D.; Leger, G.; Gaillard, J. French Patent 2 481 950, 1981; *Chem. Abstr.* 1982, 96, 104926.
- (157) Gao, Z.; Li, W.; Lu, B.; Zhang, A.; Zhou, K. *Fenzi Cuihua* 1988, 2, 101; *Chem. Abstr.* 1989, 110, 154922.
- (158) Brown, S. J.; Masters, F. A.; Vender, M. *Polyhedron* 1988, 7, 2009.
- (159) Frame, R. R. U.S. Patent 4 740 652, 1988; U.S. Patent 4 613 580, 1986; *Chem. Abstr.* 1986, 105, 211537.
- (160) Keim, W.; Behr, A.; Kraus, G. *J. Organometal. Chem.* 1983, 251, 377.
- (161) Frame, R. R.; Imai, T. U.S. Patent 4 737 480, 1988; *Chem. Abstr.* 1988, 109, 55475h.
- (162) Frame, R. R.; Barger, P. T. U.S. Patent 4 737 479, 1988; *Chem. Abstr.* 1988, 109, 55474y.
- (163) Loveless, F. C. U.S. Patent 4 642 410, 1987; *Chem. Abstr.* 1987, 106, 140993h.
- (164) Hashimoto, M.; Arakawa, T. Japanese Patent 74 00 802, 1974; *Chem. Abstr.* 1974, 81, 25021.
- (165) Isa, H.; Mandai, H.; Ukiumi, T.; Tominaga, Y.; Taniyasu, R.; Nagai, S. Japanese Patent, 79 12 952, 1979; *Chem. Abstr.* 1979, 91, 177912.
- (166) Rogov, S. A.; Kirichenko, L. N.; Verbitskii, B. G.; Prokof'ev, K. V. *Poluch. Primen. Prod. Neftekhim. M.* 1982, 123; *Chem. Abstr.* 1983, 98, 182222c.
- (167) Masagutov, R. M.; Maksimov, S. M.; Ivanov, G. E.; Ivanov, A. F.; Tolstikov, G. A.; Dzhemilev, U. M.; Tyugaev, P. F.; Svinukhov, A. G.; Masagutov, F. M. USSR Patent 992 504, 1983; *Chem. Abstr.* 1983, 99, 5179u.
- (168) Sycheva, O. A.; Melnikov, V. N.; Vladimirova, L. I. *Neftepi-erab. Neftekhim.* 1984, 9, 20.
- (169) Bobsein, R. L. U.S. Patent, 4 436 948, 1984; *Chem. Abstr.* 1984, 101, 9855.
- (170) Brennan, J. A. *Ind. Eng. Chem. Prod. Res. Dev.* 1980, 19, 2.
- (171) Yuffa, A. Y.; Verashina, L. I.; Furman, D. B.; Bragin, O. V. *Neftekhimija* 1985, 25, 495.
- (172) Avdeikina, E. G.; Tlenkopschev, M. A.; Korshak, Yu. V. *Vysokomol. Soedin., Ser. A* 1986, 28, 552.
- (173) Minsker, V.; Kirillov, A. P.; Plisov, A. V. *Khim. Tekhnol. Topl. Masel* 1977, 27.
- (174) Higashimura, T.; Miyoshi, Y.; Hasegawa, H. *J. Appl. Polym. Sci.* 1982, 27, 2593.
- (175) Hasegawa, H.; Higashimura, T. *J. Appl. Polym. Sci.* 1982, 27, 171.
- (176) Higashimura, T. Japanese Patent 58 77 827, 1983; *Chem. Abstr.* 1983, 99, 70181.
- (177) Sstartseva, G. P.; Matkovskiy, P. E.; Kuzaev, A. I.; Mel'nikov, V. N. *Neftekhimija* 1988, 28, 53.
- (178) Loveless, C. F. U.S. Patent, 4 469 910, 1984; *Chem. Abstr.* 1985, 101, 192666.
- (179) Merjianian, A. V. Eur. Pat. Appl. 137 574, 1985; *Chem. Abstr.* 1985, 103, 71820.
- (180) Berlin, A. A.; Minsker, K. S.; Prokof'ev, K. V.; Prochukhan, Yu. A.; Sangalov, Yu. A.; Kotov, S. V.; Yasinenko, V. A. *Neftepi-erab. Neftekhim.* 1988, No. 2, 25.
- (181) Prokof'ev, K. V.; Kotov, S. V.; Sangalov, Yu. A.; Kankaeva, I. N. *Neftepi-erab. Neftekhim.* 1988, No. 8, 22.
- (182) Mandai, H.; Timinaga, A.; Yoshimura, Y.; Isa, H. German Patent 2 837 235, 1979; *Chem. Abstr.* 1979, 91, 60046.
- (183) Isa, H.; Ukigai, T.; Tominaga, A.; Sato, M. Japanese Patent 76 122 002, 1975; *Chem. Abstr.* 1977, 86, 105905.
- (184) Dressler, F. H.; Vermaire, S. *Makromol. Chem., Macromol. Symp.* 1988, 13-14; 271-81.

- (185) Nippon Oil Co. Ltd., Japanese Patent 58 213 725, 1983; *Chem. Abstr.* 1984, 100, 13975.
- (186) Watts, W. L.; Marquis, E. T. U.S. Patent 4 413 156, 1983; *Chem. Abstr.* 1984, 100, 9822.
- (187) Morganson, N. E.; Vayda, A. V. Eur. Patent Appl. 0 077 113, 1986; *Chem. Abstr.* 1983, 99, 73631; U.S. Patent 4 409 415, 1983; *Chem. Abstr.* 1984, 100, 5824.
- (188) Eastham, A. M. *Can. J. Chem.* 1981, 59, 2621.
- (189) Booth, R. E.; Evans, F. E.; Eibeck, R. E.; Robinson, M. A. U.S. Patent 4 227 027, 1980; *Chem. Abstr.* 1981, 94, 30326.
- (190) Heublein, G.; Albrecht, G.; Kuempfel, W. *Acta Polym.* 1984, 35, 220.
- (191) Morganson, N. E.; Bercik, P. G. U.S. Patent 4 429 177, 1984; *Chem. Abstr.* 1984, 100, 36916a.
- (192) O'Hara, M. J.; Imai, T. U.S. Patent 4 490 571, 1984; *Chem. Abstr.* 1985, 102, 36916v.
- (193) Nadgavkar, A. M.; Swift, H. E. *Ind. Eng. Chem. Prod. Res. Dev.* 1983, 22, 675; U.S. Patent 4 394 296; 1983; *Chem. Abstr.* 1983, 99, 111523.
- (194) Morganson, N. E. U.S. Patent 4 365 105, 1982; *Chem. Abstr.* 1983, 98, 106777x.
- (195) Shubkin, R. L.; Baylerian, M. S.; Maler, A. R. *Prepr.—Am. Chem. Soc., Div. Petrol. Chem.* 1979, 24, 809.
- (196) Minachev, K. M.; Udaltsova, E. A.; Dergachev, A. A.; Mishin, I. V. *Neftekhimiya* 1988, 28, 164.
- (197) Kucherov, A. W.; Slinkin, A. A.; Kharkon, M. S.; Bondarenko, T. N.; Minachev, K. M. *Kinet. Kataliz* 1989, 30, 193.
- (198) Kustov, L. M.; Kondrat'ev, D. A.; Borovkov, T. B.; Kazanskiy, V. B.; Minachev, K. M. *Kinet. Kataliz* 1989, 30, 169.
- (199) Datka, J. *J. Chem. Soc., Faraday Trans. 1* 1981, 77, 2633.
- (200) Datka, J. *Zeolites* 1981, 1, 113; *Zesz. Nauk. Uniw. Jagiellon. Pr. Chem.* 1985, 29, 77; *Getoger. Katal.* 1983, 1, No. 5 381.
- (201) Müller, U.; Keim, W.; Krüger, C.; Betz, P. *Angew. Chem.* 1989, 101, 1066.
- (202) Chester, A. W. U.S. Patent 4 517 399, 1985; *Chem. Abstr.* 1983, 99, 197823u; Eur. Pat. 89 825, 1983.
- (203) Kaminsky, W.; Ahlers, A.; Möller-Lindenhof, N. *Angew. Chem.* 1989, 101, 1304.
- (204) Haw, J. F.; Richardson, B. R.; Oshiro, I. S.; Lazo, N. D.; Speed, J. A. *J. Am. Chem. Soc.* 1989, 111, 2052.
- (205) Motz, M. U.S. Patent 4 435 606, 1984; *Chem. Abstr.* 1984, 101, 9089x.
- (206) Threnkel, R. S. U.S. Patent 4 677 241, 1987; *Chem. Abstr.* 1987, 107, 199108x.
- (207) Xu, Z. *Shiyu Huagong* 1985, 14, 711; *Chem. Abstr.* 1986, 104, 151229y.
- (208) Langer, A. W. U.S. Patent 4 486 615, 1984; *Chem. Abstr.* 1985, 103, 149940p.
- (209) Mel'nikov, V. N.; Golubiev, V. K.; Mischenko, O. A.; Shuraev, A. N.; Abramova, L. A.; Pushkina, T. A. *Khim. Prom.* 1979, 592.
- (210) Langer, A. W. *Prepr.—Am. Chem. Soc., Div. Petrol. Chem.* 1972, 17, B119.
- (211) Langer, A. W. U.S. Patent 3 662 021, 1972; Netherlands Patent 6 601 059, 1967; *Chem. Abstr.* 1967, 66, 19045c.
- (212) Langer, A. W. U.S. Patent 3 441 630, 1970; Netherlands Patent 6 601 059, 1967; *Chem. Abstr.* 1967, 66, 19043c; U.S. Patent 3 647 912, 1972; British Patent 112 569, 1968; *Chem. Abstr.* 1968, 69, 11956a; U.S. Patent 3 629 355, 1972; Brit. Patent 920 145, 1963; *Chem. Abstr.* 1963, 58, 13691d.
- (213) Langer, A. W. U.S. Patent 3 655 812, 1972; German Patent 2 009 439, 1970; *Chem. Abstr.* 1970, 73, 121061.
- (214) Cull, N. L.; Bearden, R. U.S. Patent 3 637 897, 1972; German Patent 2 009 439, 1970; *Chem. Abstr.* 1970, 73, 121061m.
- (215) Buben, D.; Bearden, R.; Wristers, H. J. U.S. Patent 3 862 257, 1975; *Chem. Abstr.* 1975, 83, 119115.
- (216) Favis, D. V. German Patent 1 948 992, 1969; *Chem. Abstr.* 1971, 75, 21488a.
- (217) Matkovskiy, P. E.; D'yachkovskiy, F. S. USSR Patent 536 155, 1976; *Chem. Abstr.* 1977, 86, 139378.
- (218) Cull, N. L.; Bearden, R., Jr.; Mertzweiller, J. K. Ger. Offen Patent 1 960 793, 1970; *Chem. Abstr.* 1970, 73, 56575.
- (219) Arakawa, T.; Saeki, K.; Sato, Y.; Kitazawa, Y. U.S. Patent 3 725 497, 1973; Ger. Patent 1 949 878, 1970; *Chem. Abstr.* 1971, 74, 53005q.
- (220) Arakawa, T.; Saeki, K.; Sato, Y.; Kitazawa, Y. U.S. Patent 3 652 705, 1972; German Patent 1 949 878, 1970; *Chem. Abstr.* 1971, 74, 53005q.
- (221) Iwakuni, T. A.; Sato, Y. U.S. Patent 3 660 519, 1972; German Patent 2 041 487, 1971; *Chem. Abstr.* 1971, 75, 140214w.
- (222) Mravec, D.; Lacny, Z.; Ilavsky, J. *Ropa Uhlie* 1986, 28, 283.
- (223) Butter, S. A. U.S. Patent 3 981 941, 1976; *Chem. Abstr.* 1976, 85, 176805k.
- (224) Cull, N. L.; Bearden, R., Jr.; Mertzweiller, J. K. German Offen Patent 1 960 778, 1970; *Chem. Abstr.* 1971, 75, 56575.
- (225) Arakawa, T.; Sato, Y.; Kitazawa, Y. German Patent 1 949 878, 1970; *Chem. Abstr.* 1971, 74, 53005.
- (226) Matkovskiy, P. E.; Pomagailo, A. D.; Russiyan, L. N.; Lisitskaya, A. P.; D'yachkovskiy, F. S.; Brikenstein, K. A.; Gerasina, M. P. USSR Patent 491 404, 1975; *Chem. Abstr.* 1976, 84, 89577y.
- (227) Mamedaliev, G. A.; Aliev, V. S.; Aliev, C. M.; Azizov, A. G.; Aliev, A. B.; Askierova, E. O. USSR Patent 1 234 392, 1986; *Chem. Abstr.* 1986, 105, 173231r.
- (228) Henrić-Olivé, G.; Olivé, S. German Patent 1 924 427, 1970; *Chem. Abstr.* 1970, 73, 5743; Brit. Patent 1 228 292, 1974; *Chem. Abstr.* 1971, 75, 21452n.
- (229) Kuliev, R. S.; Akhmedov, V. M.; Gassanova, A. A.; Pirmedov, G. USSR Patent 1 214 734, 1986; *Chem. Abstr.* 1986, 105, 26977k.
- (230) Shiraki, Y.; Kono, S. Japanese Patent 62 59 225, 1987; *Chem. Abstr.* 1987, 107, 58489h.
- (231) Shiraki, Y.; Kono, S. Japanese Patent 62 00 430, 1987; *Chem. Abstr.* 1987, 107, 7812c.
- (232) Shiraki, Y.; Kawano, Ah.; Takeuchi, K. Eur. Pat. Appl. 241 596, 1987; *Chem. Abstr.* 1988, 108, 56784z.
- (233) Langer, A. W. U.S. Patent 4 410 750, 1983; U.S. 4 377 723, 1983; *Chem. Abstr.* 1983, 98, 198893k.
- (234) Young, D. A.; Jones, L. O.; Campione, T. J. Eur. Pat. Appl. 295 960, 1988; *Chem. Abstr.* 1989, 110, 173979u.
- (235) Langer, A. W. U.S. Patent 4 409 414, 1983; Netherlands Patent 6 601 059, 1966; *Chem. Abstr.* 1967, 66, 19045.
- (236) Langer, A. W. U.S. Patent 4 434 313, 1984; U.S. Patent 4 377 720, 1983; *Chem. Abstr.* 1983, 98, 98893h.
- (237) Langer, A. W.; Doyle, G.; Burkhardt, T. J.; Looney, R. W. U.S. Patent 4 409 409, 1983; *Chem. Abstr.* 1984, 100, 8952r.
- (238) Attridge, Ch. J.; Jones, E.; Pioli, A. J.; Wilkinson, P. J. German Patent 2 219 048, 1973; *Chem. Abstr.* 1973, 78, 135609.
- (239) Kuliev, R. S.; Akhmedov, V. USSR Patent 1 073 279, 1984; *Chem. Abstr.* 1984, 100, 212821.
- (240) Longi, P.; Greco, F.; Rossi, U. Italian Patent 871 096, 1973; *Chem. Abstr.* 1973, 78, 148475d.
- (241) Japanese Patent 58 201 729, 1983; *Chem. Abstr.* 1984, 100, 174258c.
- (242) Khodakovskaya, V. A.; Dyachkovskiy, F. S. PCT Int. Appl. 80 00 224, 1980; *Chem. Abstr.* 1980, 93, 72615x.
- (243) Attridge, C. J.; Jackson, R.; Maddock, S. J.; Thompson, D. T. *J. Chem. Soc., Chem. Commun.* 1973, 132.
- (244) Mamedaliev, G. A.; Azizov, A. G.; Aliev, W. C.; Dzanibekov, N. F. USSR Patent SU 1351912, 1987; *Chem. Abstr.* 1988, 108, 222266c.
- (245) Davis, D. V. U.S. Patent 2 549 723, 1970; *Chem. Abstr.* 1971, 74, 124766b.
- (246) Mason, R. F. U.S. Patent 3 676 523, 1972; *Chem. Abstr.* 1972, 77, 100710q.
- (247) Mason, R. F. U.S. Patent 3 686 351, 1972; *Chem. Abstr.* 1972, 77, 151422e.
- (248) Mason, R. F. U.S. Patent 3 737 475, 1973; *Chem. Abstr.* 1973, 79, 31448u.
- (249) Bauer, R. S.; Chung, M.; Glockner, P. W.; Keim, W.; Zwet, H. U.S. Patent 3 644 563, 1972; *Chem. Abstr.* 1971, 75, 110729a.
- (250) Arakawa, T.; Saeki, K. Japanese Patent 7 222 208, 1972; *Chem. Abstr.* 1972, 77, 100694s.
- (251) Lutz, E. U.S. Patent 3 825 615, 1974; *Chem. Abstr.* 1974, 81, 119, 895.
- (252) O'Donnell, A. E. U.S. Patent 4 260 844, 1981; *Chem. Abstr.* 1981, 95, 61445g.
- (253) Smidt, K. F.; Mironova, L. V.; Tkach, V. S. USSR Patent 654 594, 1979; *Chem. Abstr.* 1979, 91, 85671h.
- (254) Meyer, J. G. U.S. Patent 4 111 834, 1978; *Chem. Abstr.* 1979, 90, 122272.
- (255) Meyer, J. G. U.S. Patent 4 117 022, 1978; *Chem. Abstr.* 1979, 90, 54472b.
- (256) Singleton, D. M. U.S. Patent 4 472 522, 1984; *Chem. Abstr.* 1985, 102, 46405p.
- (257) Singleton, D. M. Eur. Patent Appl. 128 597, 1985; *Chem. Abstr.* 1985, 102, 46405.
- (258) Murray, R. E. U.S. Patent 4 689 437, 1987; *Chem. Abstr.* 1988, 108, 6646k.
- (259) Singleton, D. M. U.S. Patent 4 503 279, 1985; *Chem. Abstr.* 1985, 102, 46405p.
- (260) Singleton, D. M. U.S. Patent 4503 280, 1985; *Chem. Abstr.* 1985, 102, 85118s.
- (261) Singleton, D. M. European Patent Appl. 128 596, 1985; *Chem. Abstr.* 1985, 102, 85118c.
- (262) Kister, A.; Lutz, E. F. U.S. Patent 4 020 121, 1977; *Chem. Abstr.* 1977, 87, 6654j.
- (263) Seidov, N. H.; Dalin, M. A.; Kyazimov, S. M. German Offen Patent 2 640 194, 1976; *Chem. Abstr.* 1978, 88, 153303t.
- (264) Lutz, E. F.; Gautier, P. A. Eur. Patent Appl. 177 999, 1986; *Chem. Abstr.* 1986, 105, 62701r.
- (265) Lutz, E. F. U.S. Patent 4 528 416, 1985; *Chem. Abstr.* 1986, 104, 6317w.
- (266) Seidov, N. M.; Dalin, M. USSR Patent 545 141, 1979; *Chem. Abstr.* 1979, 91, 158368q.
- (267) Gene, N.; Harold, D. L. U.S. Patent 2 965 408, 1960; *Chem. Abstr.* 1961, 55, 16009.
- (268) Brown, S. J.; Masters, A. F. *J. Organometal. Chem.* 1989, 367, 371.
- (269) Tada, A.; Suzuka, H.; Imizu, Y. *Chem. Lett.* 1987, 2, 423.

- (270) Ono, N.; Murakami, T.; Miki, M. *Japan Kokai* 62 142 125, 1987; *Chem. Abstr.* 1988, 108, 76065u.
- (271) Zhavaronkov, M. N.; Darogochinskii, A. Z.; Nadirov, A. A. *Neftekhimiya* 1983, 23, 495.
- (272) Pshevalskaya, L. K.; Furman, D. B.; Shvets, V. A.; Dzukovskii, S. S.; Kharitonova, T. M.; Bondarenko, G. N.; Taber, A. M.; Kazanskii, V. B.; Bragin, O. V.; Kalechic, I.; Vasserberg, V. E. *Kinet. Katal.* 1978, 19, 1283.
- (273) Furman, D. B.; Kharitonova, T. M.; Dzukovskii, S. S.; Nechaeva, T. I.; Fedorov, B. M.; Taber, A. M.; Lipovich, V. G.; Bragin, O. G.; Kalechic, I. V.; Vasserberg, V. E. *Izv. Akad. Nauk. SSSR* 1979, 10, 2278.
- (274) Furman, D. B.; Kalechic, I. V.; Makhlis, L. A.; Volchkov, N. V.; Taber, A. M.; Bragin, O. V.; Vasserberg, V. E. *Izv. Akad. Nauk SSSR* 1981, 3, 673.
- (275) Knudsen, R.; Reiter, S. U.S. Patent 4 482 640, 1984; *Chem. Abstr.* 1985, 102, 79447q.
- (276) Haensle, P. German Offen Patent 2 902 203, 1980; *Chem. Abstr.* 1981, 94, 65831.
- (277) Haensle, P. German Offen Patent 3 027 782, 1982; *Chem. Abstr.* 1982, 96, 142246r.
- (278) Behr, A.; Falbe, V.; Freudenberg, V.; Keim, W. *Isr. J. Chem.* 1986, 27, 277.
- (279) Glockner, P. W.; Keim, W.; Mason, R. F.; Bauer, R. S. German Offen Patent 2 053 758, 1971; *Chem. Abstr.* 1971, 75, 88072g.
- (280) Zwet, H.; Bauer, R.; Keim, W. U.S. Patent 3 644 564, 1972; *Chem. Abstr.* 1971, 75, 98942e.
- (281) Van Zwet, H.; Bauer, S. R.; Keim, W. German Offen Patent 2 062 293, 1971; *Chem. Abstr.* 1971, 75, 98942e.
- (282) Van Zwet, H.; Keim, W. U.S. Patent 3 635 937, 1972; *Chem. Abstr.* 1971, 75, 110729a.
- (283) Tsvetkov, O. N.; Toporishcheva, R. L.; Bogdanov, S. K. USSR Patent US 711 044, 1980; *Chem. Abstr.* 1980, 92, 129655u.
- (284) Shell Int. Res., Neth. Appl. 70 16 039, 1971; *Chem. Abstr.* 1971, 75, 110729.
- (285) Shell Intern. Res. Neth. Appl., 70 16 037, 1971; *Chem. Abstr.* 1971, 75, 110727p.
- (286) Glockner, P. W.; Keim, W.; Mason, R. F. U.S. Patent 3 647 914, 1972; *Chem. Abstr.* 1971, 75, 88072d.
- (287) Bauer, R. S.; Glockner, P. W.; Keim, W.; Mason, R. F. U.S. Patent 3 647 915, 1972; *Chem. Abstr.* 1971, 75, 88072d.
- (288) Shell Oil Co. U.S. Patent 3 686 159, 1972; *Chem. Abstr.* 1972, 76, 15196m.
- (289) Beach, D. L.; Harrison, J. J. U.S. Patent 4 377 529, 1983; *Chem. Abstr.* 1983, 98, 6873; U.S. Patent 4 377 528, 1983; *Chem. Abstr.* 1983, 99, 5824a; Eur. Pat. Appl. 52 930, 1982; *Chem. Abstr.* 1982, 97, 163257f; Eur. Pat. Appl. 52 931, 1982; *Chem. Abstr.* 1982, 97, 163256e.
- (290) Pauckert, M.; Keim, W. *Organometallic* 1983, 2, 594.
- (291) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, K. *Angew. Chem.* 1978, 90, 493.
- (292) Keim, W.; Kowaldt, F. H. *Erdol Kohle, Erdgas, Petrochem.* 1978, 78, 453.
- (293) Farley, F. F. U.S. Patent 3 647 906, 1972; *Chem. Abstr.* 1972, 76, 112646n.
- (294) Keim, W.; Kowaldt, F. H. *Compend. Dtech. Ges. Mineralog. Chem.* 1978, 78, 453; *Chem. Abstr.* 1980, 93, 7580t.
- (295) Beach, D. L.; Harrison, J. J. U.S. Patent 4 394 322, 1983; *Chem. Abstr.* 1983, 99, 176066j; U.S. Patent 4 301 318, 1982; *Chem. Abstr.* 1982, 96, 6873w; U.S. Patent 4 310 716, 1982; *Chem. Abstr.* 1982, 96, 180743h; U.S. Patent 4 293 727, 1982; *Chem. Abstr.* 1982, 96, 34516s; U.S. Patent 4 293 502, 1982; *Chem. Abstr.* 1982, 96, 6873w.
- (296) Beach, D. L.; Kobyliński, T. P. U.S. Patent 4 288 648, 1981; *Chem. Abstr.* 1981, 95, 219764x.
- (297) Beach, D. L.; Kobyliński, T. P. U.S. Patent 4 272 407, 1981; *Chem. Abstr.* 1981, 95, 50232n.
- (298) Beach, D. L.; Kobyliński, T. P. U.S. Patent 4 272 406, 1981; *Chem. Abstr.* 1981, 95, 50233.
- (299) Beach, D. L.; Kobyliński, T. P. *J. Chem. Soc., Chem. Commun.* 1980, 19, 933.
- (300) Barnett, K. W.; Glockner, P. W. Ger. Offen 2001102, 1970; *Chem. Abstr.* 1970, 73, 77852.
- (301) Barnett, K. W.; Raley, J. H. U.S. Patent 3 532 765, 1970; *Chem. Abstr.* 1970, 73, 120047z.
- (302) Barnett, K. W. U.S. Patent 3 527 838, 1970; *Chem. Abstr.* 1970, 73, 77852.
- (303) Miller, S. J. U.S. Patent 4 608 459, 1986; *Chem. Abstr.* 1986, 105, 156044n.
- (304) Aliev, V. S.; Mirzoeva, Z. S.; Soldatova, V. A. *Sb. Tr. Inst. Neftekhim. Protsessov im. Yu. G. Mamedaliev, Akad. Nauk Az SSR* 1986, 15, 89; *Chem. Abstr.* 1987, 106, 17827t.
- (305) Fowler, A. E.; White, G. E.; Sims, S. A. U.S. Patent 4 380 684, 1983; *Chem. Abstr.* 1983, 99, 6223r.
- (306) Shewbart, W. E.; Sims, S. A.; Head, B. D.; White, G. E. U.S. Patent 4 314 090, 1982; *Chem. Abstr.* 1982, 96, 103613p.
- (307) Keim, W. *Homogeneous-Heterogeneous Catalysis, Proc. Int. Symp. Relat. Homogeneous Heterog. Catal.* 1986, 5, 499.
- (308) Hunt, M. W. U.S. Patent 3 217 058, 1964; *Chem. Abstr.* 1966, 64, 1954b.
- (309) Le Page, J. F.; Cosyns, J.; Juguin, M. J.; Miguel, J. Belg. Patent 874 821, 1978; *Chem. Abstr.* 1980, 92, 131848e.
- (310) Aliev, V. S.; Mirzoeva, Z. Sh.; Kagramanov, E. E. *Sb. Tr. Inst. Neftekhim. Protsessov im. Yu. G. Mamedaliev, Akad. Nauk Az SSR* 1982, 13, 167; *Chem. Abstr.* 1983, 99, 23011n.
- (311) Ethyl. Corp. U.S. Patent 3 663 647, 1972; *Chem. Abstr.* 1972, 77, 100688h.
- (312) Gulf Research, U.S. Patent 3 702 345, 1973; *Chem. Abstr.* 1973, 78, 29199t.
- (313) Serratore, J. U.S. Patent 3 499 057, 1970; *Chem. Abstr.* 1970, 72, 99987e.
- (314) Gulf Research, U.S. Patent 3 502 741, 1970; *Chem. Abstr.* 1970, 73, 5724f.
- (315) Ziegler, K.; Brit. Patent 777 152, 1957; *Chem. Abstr.* 1957, 51, 12543.
- (316) Ziegler, K.; Wilke, G.; Holzkamp, E. U.S. Patent 2 781 411, 1957; *Chem. Abstr.* 1957, 51, 5380f.
- (317) Ziegler, K.; Gellert, H. G.; Holzkamp, E.; Wilke, G.; Duck, E. W.; Kroll, W. R. *Ann.* 1960, 629, 172.
- (318) Pol, P. Z.; Rayer, D. J. U.S. Patent 4 455 289, 1985; *Chem. Abstr.* 1984, 101, 132954r.
- (319) Raffinage, C. F.; Neth. Appl. 6 405 301, 1965; *Chem. Abstr.* 1965, 62, 7888e.
- (320) Seidov, M. N.; Kyazimov, S. M.; Mamedyavov, M. A.; Guseinov, A. P.; Kuliev, T. M. *Japan Kokai* 78 57 289, 1978; *Chem. Abstr.* 1978, 89, 75663.
- (321) Seidov, M. N.; Kyatimov, S. M.; Mamedyavov, M. A.; Guseinov, A. P.; Kuliev, T. M. Ger. Offen. 2 650 585, 1977; *Chem. Abstr.* 1978, 89, 44433h.
- (322) Sen, A.; Lai, T. *J. Am. Chem. Soc.* 1981, 103, 4627.
- (323) Heveling, J. Ger. Offen. DE 3 741 302, 1988; *Chem. Abstr.* 1988, 109, 7646v.
- (324) Anshits, A. G.; Vereshchagin, S. N.; Korniets, E. D.; Kholopova, G. D.; Holl, V. K. *Kinet. Katal.* 1988, 29, 626.
- (325) Heveling, J.; Van der Beek, A.; De Pender, H. *Appl. Catal.* 1988, 42, 325.
- (326) Podall, H. E.; Foster, W. E.; Giraitis, A. P. *J. Org. Chem.* 1958, 23, 81.
- (327) MecLlin, A. S.; Borekov, V. V.; Kazanskii, V. B. *Dokl. Akad. Nauk. SSSR* 1986, 286, 914.
- (328) Kubelkova, L.; Novakova, J.; Wichterova, B.; Jiru, P. *Collect. Czech. Chem. Commun.* 1980, 45, 2290.
- (329) Lange, J. P.; Gutsze, A.; Allgeier, J.; Karge, H. G. *Appl. Catal.* 1988, 45, 345.
- (330) OP Inc. Fr Demande 2 402 478, 1979; *Chem. Abstr.* 1979, 91, 92277a.
- (331) Kviale, S.; Blindheim, U.; Ellestad, O. H. *J. Mol. Catal.* 1984, 26, 341.
- (332) Immergut, E. H.; Kollman, G.; Malatesta, A. *J. Polym. Sci.* 1961, 51, S-57.
- (333) Bogdanovic, B.; Spliethoff, B.; Wilke, G. *Angew. Chem.* 1980, 92, 633.
- (334) Watts, L. W., Jr.; Marquis, E. T. U.S. Patent 4 367 352, 1983; *Chem. Abstr.* 1982, 97, 185195k.
- (335) Datka, J.; Drelinkiewicz, A.; Malecka, A. *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* 1976, 24, 137.
- (336) Netherland Patent, 6 409 179, 1965; *Chem. Abstr.* 1965, 63, 5770h.
- (337) Wilke, G. Belgium Patent 651 596, 1965; *Chem. Abstr.* 1966, 64, 9928b.
- (338) Belgium Patent, 874 819, 1978; *Chem. Abstr.* 1980, 92, 75810.
- (339) Chauvin, Y.; Cornereuce, D.; Gaillard, J. Eur. Patent, 12 685, 1980; *Chem. Abstr.* 1981, 94, 16361v.
- (340) Yoo, Y. S.; Milam, R. L. U.S. Patent 3 954 668, 1976; *Chem. Abstr.* 1976, 85, 48409x.
- (341) Sachinidis, S. J.; Clutterbuck, L. M.; Masters, A. F.; Brown, S. J.; Tregloan, P. A. *Appl. Catal.* 1989, 48, 1.
- (342) Anderson, J. R.; Chang, Y. F.; Western, R. J. *J. Catal.* 1989, 118, 466.
- (343) Ferraris, G.; Prida, A.; Cesca, S. German Offen. 2 831 554, 1959; *Chem. Abstr.* 1979, 90, 139977a.
- (344) U.S. Patent, 2 870 217, 1959 (see ref 103).
- (345) Ohtsuka, H.; Tomita, N.; Sato, H. *Mem. Fac. Eng. Hokkaido Univ.* 1950, 8 (1), 23; *Chem. Abstr.* 1952, 46, 6075f.
- (346) British Patent 696 568, 1953 (see ref 103); U.S. Patent 2 500 307, 1950 (see ref 103); U.S. Patent 2 814 655, 1957 (see ref 103); U.S. Patent 2 486 533, 1949 (see ref 103); U.S. Patent 3 041 386, 1962 (see ref 103); U.S. Patent 3 046 316, 1962 (see ref 103); U.S. Patent 2 755 324, 1956 (see ref 103); Muchinskii, D. Ja. *Izvest. Akad. Nauk Turkmen. SSR, Ser. fiz. techn.* 1960, 6, 58; *Chem. Abstr.* 1961, 55, 15902e; German Offen. 939 149, 1956 (see ref 103); U.S. Patent 2 517 720, 1950 (see ref 103); U.S. Patent 2 952 428, 1962 (see ref 103); British Patent 681 042, 1952 (see ref 103).
- (347) Abdrakhimov, Yu. R. *Zh. F. Galimov, Khim. Tekhnol. Topl. Masel.* 1975, 16; *Chem. Abstr.* 1976, 85, 108193p.
- (348) Pasky, J. Z. U.S. Patent 4 444 985, 1984; *Chem. Abstr.* 1984, 101, 55658e.

- (349) U.S. Patent 2 766 312, 1956 (see ref 103).
(350) U.S. Patent 2 528 876, 1950 (see ref 103).
(351) Robert, M. U.S. Patent 3 932 553, 1976; *Chem. Abstr.* 1976, 84, 164119c.
(352) U.S. Patent 3 071 634, 1963 (see ref 103).
(353) U.S. Patent 2 525 787, 1950 (see ref 103).
(354) Fontana, C. M. *Cationic Polym. Relat. Complexes, Proc. Conf.* 1952, 121; *Chem. Abstr.* 1954, 48, 5625d.
(355) U.S. Patent 2 458 818, 1949 (see ref 103).
(356) U.S. Patent 3 193 596, 1965 (see ref 103).
(357) *Petrol. Refiner* 1954, 33, 193; J. D. Waddell, *Oil Gas* 1941, August; J. H. Steffens, M. V. Zimmerman, H. J. Laituri, *J. Chem. Progr.* 1949, 45, 269.
(358) Clark, A. *Ind. Eng. Chem.* 1953, 45, 1476.
(359) Imai, T. U.S. Patent 4 463 212, 1984; *Chem. Abstr.* 1984, 101, 170687a.
(360) Garwood, W. E. *Prep.—Am. Chem. Soc., Div. Petrol. Chem.* 1982, 27, 563.
(361) Tabak, S. A.; Krambeck, F. J.; Garwood, W. E. *AIChE J.* 1986, 32 (9), 1526; *Chem. Abstr.* 1986, 105, 13624a.
(362) Mangasaryan, N. A.; Kostrich, L. P.; Savadin, E. K.; Mamedova, V. M.; Askerov, N. L.; Putlin, N. E.; Mukhamedov, M. N. *Khim. Tekhnol. Topl. Masel.* 1988, 6, 6; *Chem. Abstr.* 1988, 109, 93685j.
(363) Rafikov, S. R.; Yudaev, A. L.; Minsker, Z. I.; Svinukov, A. G.; Kirillov, A. P.; Nel'kenbaum, Y. Y. USSR Patent 690 024, 1979; *Chem. Abstr.* 1980, 92, 75811y.
(364) Zhang, S. Faming Zhuanyi Shenging Gongkai Shuomingshu CN 87 101 742, 1988; *Chem. Abstr.* 1989, 110, 135923p.
(365) Giusti, A.; Gusi, S.; Bellussi, G.; Fattore, V. European Patent Appl. EP 293 950, 1988; *Chem. Abstr.* 1989, 110, 155048k.
(366) Giusti, A.; Gusi, S.; Bellussi, G.; Fattore, V. European Patent Appl. EP 290 068, 1988; *Chem. Abstr.* 1989, 110, 115529m.
(367) Mirotsuke, E. I.; Niihamashi, Y. N. U.S. Patent 3 586 734, 1971; *Chem. Abstr.* 1970, 72, 12037a.
(368) La Pierre, B.; Wong, S. S. U.S. Patent 4 430 516, 1984; *Chem. Abstr.* 1984, 100, 123892h.
(369) Blain, D. A.; Page, M. N.; Young, L. B. European Patent Appl. EP 311 310, 1989; *Chem. Abstr.* 1989, 111, 40133n.
(370) Bercik, P. G.; Metzger, J. K.; Swift, H. E. *Ind. Eng. Chem. Prod. Res. Dev.* 1978, 17, 214.
(371) Epinoza, R. L.; Scurell, M. S.; Van Walsen, H. J. *Chem. Lett.* 1984, 10, 1781.
(372) Bugai, E. A.; Galiakbarov, M. F. USSR Patent 711 041, 1980; *Chem. Abstr.* 1980, 92, 129656r.
(373) Guth, L. J.; Faust, A. G.; Raatz, F.; Lamblin, J. M. European Patent Appl. EP 269 503, 1988; *Chem. Abstr.* 1988, 109, 150248f.
(374) Occelli, M. L.; Hsu, J. T.; Galya, L. G. *J. Mol. Catal.* 1985, 32, 377.
(375) U.S. Patent 4 613 719, 1986; *Chem. Abstr.* 1986, 105, 229678m.
(376) Beach, D. L.; Kobylinski, T. P. U.S. Patent 4 293 726, 1981; *Chem. Abstr.* 1982, 96, 34516v.
(377) Beach, D. L.; Kissin, Y. V. U.S. Patent 4 686 315, 1987; *Chem. Abstr.* 1987, 107, 219470q.
(378) Beach, D. L.; Harrison, J. J. U.S. Patent 4 382 153, 1983; *Chem. Abstr.* 1983, 99, 21935t.
(379) Gao, Z.; Zhang, A.; Zhou, J. Y. K. *Yingyong Huaxue* 1987, 4(1), 40; *Chem. Abstr.* 1987, 106, 176924a.
(380) Cares, W. R. U.S. Patent 4 065 512, 1977; *Chem. Abstr.* 1978, 89, 6805a.
(381) Chauvin, Y.; Commereuc, D.; Gaillard, J.; Phung, N. H. U.S. Patent 4 387 262, 1983; *Chem. Abstr.* 1981, 94, 16361r.
(382) Saeki, K.; Ono, N.; Murakami, T. Japan Kokai, JP 61 151 136, 1986; *Chem. Abstr.* 1987, 106, 4515b.
(383) Austin, R.; Beach, L. D.; Pellerini, J. P. U.S. Patent 4 319 065, 1982; *Chem. Abstr.* 1982, 96, 165400a.
(384) Subbotin, A. N.; Khodakov, V.; Anders, K.; Nakhshunov, V. S. *Izv. Akad. Nauk. SSSR Ser. Khim.* 1981, 8, 1724.
(385) Loveless, F. C.; Merijanjan, A. V.; Smudin, D. J.; Nudenberg, W. European Patent EP 139 343, 1985; *Chem. Abstr.* 1985, 103, 105433a.
(386) Helbig, M.; Hartung, M.; Kuempfel, W.; Stadermann, D. German (East) DD 154 983, 1982; *Chem. Abstr.* 1982, 97, 198721e.
(387) Juguin, B.; Miguel, J.; Martino, G. French Demande 2 493 306, 1982; *Chem. Abstr.* 1982, 97, 128270h.
(388) Kitamura, T.; Tamura, M. Japan Kokai 79 66 993, 1979; *Chem. Abstr.* 1979, 91, 124211b.
(389) Tsvetkov, O. N.; Zhernokleeva, N. A. *Neftekhimiya* 1989, 29, 224.
(390) Akatsu, S. Japan Kokai 01 95 108, 1989; *Chem. Abstr.* 1989, 111, 195622v.
(391) Vlasov, A. V.; Kotov, S. V.; Prokofev, K. V.; Sangalov, Yu. A.; Koroleva, E. N. *Neftepererab., Neftekhim. (Moscow)* 1989, 2, 16; *Chem. Abstr.* 1989, 111, 195866c.
(392) Schoenthal, G. W.; Slauch, L. H. European Patent Appl. EP 257 695, 1988; *Chem. Abstr.* 1988, 109, 54952e.
(393) Van der Berg, J.; Johannes, P.; Kortbeek, A. G. T.; Grandvallet, P. European Patent Appl. EP 281 208, 1988; *Chem. Abstr.* 1988, 109, 231744s.
(394) Japan Kokai 62 72 785, 1987; *Chem. Abstr.* 1987, 106, 216854m.
(395) Busca, G.; Ramis, G. J. *Chem. Soc., Faraday Trans. 1* 1989, 85 (1), 137.
(396) Miller, S. J. U.S. Patent 4 423 268, 1983; *Chem. Abstr.* 1983, 99, 5183z; German Offen. 3 229 829, 1983; *Chem. Abstr.* 1983, 99, 5183.
(397) Slauch, L. H. U.S. Patent 4 367 361, 1982; *Chem. Abstr.* 1983, 98, 142936g.
(398) Nippon Oils and Fats Co., Ltd. Japan Kokai 81 139 430, 1981; *Chem. Abstr.* 1982, 96, 35912h.
(399) Nippon Oils and Fat Co., Ltd. Japan Kokai 81 139 428, 1981; *Chem. Abstr.* 1982, 96, 35913j.
(400) Nippon Oils and Fat Co., Ltd. Japan Kokai 81 139 429, 1981; *Chem. Abstr.* 1982, 96, 35914k.
(401) Kuliev, R. Sh.; Zulfugarov, Z. G.; Abasova, T. M.; Gasanova, R. Z.; Dzhabadov, M. W. USSR Patent 759 529, 1980; *Chem. Abstr.* 1980, 93, 189046d.
(402) Sangalov, Yu. A.; Yasman, Yu. B.; Odinokov, V. N.; Ignatyuk, V. K.; Ilkaeva, E. M.; Svinukhov, A. G.; Minsker, K. S. *Neftekhimiya* 1977, 17, 865.
(403) Panchenkov, G. M.; Vagin, M. F.; Bogdanov, D. B.; Grinin, L. M.; Kanaeva, M. G. *Zh. Fiz. Khim.* 1974, 48, 884.
(404) Brennan, J. F.; Lester, G. R. U.S. Patent 3 773 853, 1973; *Chem. Abstr.* 1974, 80, 36686u.
(405) Vybihal, J. *Sb. Pr. Vyzk. Chem. Vyuuziti Uhli Dentu Ropy* 1972, 12, 43; *Chem. Abstr.* 1973, 79, 7611q.
(406) Johnson, T. H. U.S. Patent 4 476 343, 1984; *Chem. Abstr.* 1985, 102, 281122c.
(407) Ramus, G.; Busca, G.; Lorenzelli, V.; Rossi, P. F.; Bensitel, M.; Saur, O.; Lavalley, J. C. *Proc. Int. Congr. Catal 9th* 1988, 4, 1874.
(408) Konovalchikov, L. D.; Radchenko, E. D.; Nefedov, B. K.; Rostanin, N. N. *Neftepererab. Neftekhim.* 1987, 2, 3.
(409) Hammond, K. G.; Sendra, J. C.; Watts, L. W.; Marquis, E. T. European Patent Appl. EP 136 377, 1988; *Chem. Abstr.* 1984, 100, 7184z.
(410) Allphin, N. L.; Valentine, F. S.; Grams, G. W. U.S. Patent 4 239 930, 1981; *Chem. Abstr.* 1981, 94, 159561u.
(411) Madgavkar, A. M.; Swift, H. E. U.S. Patent 4 308 411, 1981; *Chem. Abstr.* 1982, 96, 106134u.
(412) Cupples, B. L.; Heilman, W. J.; Kresqe, A. N. German Offen. 2 651 637, 1977; *Chem. Abstr.* 1977, 87, 53849m.
(413) Okumura, Y.; Shiozawa, K.; Koyano, T. Japan Kokai 78 89 089, 1978; *Chem. Abstr.* 1979, 90, 39440b.
(414) Nipe, R. N.; Schick, J. W.; Gemmill, R. M. U.S. Patent 4 225 739, 1980; *Chem. Abstr.* 1980, 93, 242436j.
(415) Cupples, B. L.; Madgavkar, A. M. U.S. Patent 4 213 001, 1980; *Chem. Abstr.* 1980, 93, 220368u.
(416) Weitkamp, J. *Proc. Int. Conf. Zeolites* 1980, 5, 858.
(417) Shubkin, R. L.; Baylerian, M. S. U.S. Patent 4 376 222, 1983; *Chem. Abstr.* 1983, 98, 197591w.
(418) Shubkin, R. L.; Baylerian, M. S.; Maler, A. R. *Ind. Eng. Chem. Prod. Res. Dev.* 1980, 19, 15.
(419) Matry, C.; Engelhard, Ph. French Demande 2 504 121, 1982; *Chem. Abstr.* 1983, 98, 125394m.
(420) Larkin, J. M. U.S. Patent 4 395 578, 1983; *Chem. Abstr.* 1983, 99, 161244s.
(421) Larkin, J. M. U.S. Patent 4 434 309, 1984; *Chem. Abstr.* 1984, 100, 194890s.
(422) Darden, J. W.; Marquis, E. T.; Watts, L. W. U.S. Patent 4 400 565, 1983; *Chem. Abstr.* 1983, 99, 175203q.
(423) Priola, A.; Gozzelino, G.; Ferrero, F. *Polym. Bull (Berlin)* 1985, 13(3), 245.
(424) Gregory, L. H. U.S. Patent 4 531 014, 1985; *Chem. Abstr.* 1984, 101, 174402b.
(425) Minachev, K. M.; Bondarenko, T. N.; Kondratev, D. A. *Izv. Akad. Nauk. SSSR, Ser. Khim.* 1987, 6, 1225.
(426) Kojima, M.; Rautenbach, M. W.; O'Connor, C. T. *Ind. Eng. Chem. Res.* 1988, 27 (2), 248.
(427) Kamiyama, S.; Shiozawa, K.; Toyozumi, T.; Kaneko, K. Canadian Patent 1 212 659, 1986; *Chem. Abstr.* 1987, 106, 50791n.
(428) O'Connor, C. T.; Fasol, R. E.; Foulds, G. A. *Fuel Process Technol.* 1986, 13, 41.
(429) Hartung, H.; Hallpap, P.; Stadermann, D.; Heublein, G.; Opfermann, J. *Wiss. Z. Friedrich-Schiller-Universität Jena. Naturwiss. Reihe* 1985, 34, 821; *Chem. Abstr.* 1986, 105, 23908c.
(430) Hartung, H.; Hellmig, R.; Heublein, G.; Rottmayer, H. H.; Schwachula, G.; Studermann, D. German (East) Patent DD 214 604, 1984; *Chem. Abstr.* 1986, 104, 5560h.
(431) Saus, A.; Schmidt, E. J. *Catal.* 1985, 94, 187.
(432) O'Hara, M.; Imai, T. U.S. Patent 4 476 342, 1984; *Chem. Abstr.* 1985, 102, 281123r.
(433) Toa, K. K. Japan Kokai 59 227 830, 1984; *Chem. Abstr.* 1985, 102, 185685t.
(434) Hashimoto, T.; Tagaya, N.; Maeshima, T.; Ueda, K.; Kokubo, M. European Patent Appl. EP 90 569, 1982; *Chem. Abstr.* 1984, 100, 34978y.
(435) Nippon Oil Co. Japan Kokai 59 212 438, 1984; *Chem. Abstr.* 1985, 102, 167321f.

- (436) Gibadullina, Kh. M.; Galimov, Z. F. *Izv. Vyssh. Uchebn. Zaved. Neft. Gaz.* 1983, 26, 38; *Chem. Abstr.* 1983, 99, 38833f.
- (437) Manning, H. E. French Demande 2 492 812, 1982; *Chem. Abstr.* 1982, 97, 128285s.
- (438) Juguin, B.; Cosyns, J.; Le Page, J. F.; Miguel, J. British Patent 2 006 263, 1979; *Chem. Abstr.* 1979, 91, 195750d.
- (439) Yoo, J. S.; Sun, J.; Erickson, H. British Patent 1 411 692, 1975; *Chem. Abstr.* 1976, 84, 60247e.
- (440) Miller, S. J. U.S. Patent 4 542 251, 1985; *Chem. Abstr.* 1986, 104, 19322u.
- (441) Rodewald, P. G. U.S. Patent 4 751 341, 1988; *Chem. Abstr.* 1986, 104, 152151d.
- (442) Tabak, S. A. U.S. Patent 4 254 295, 1981; *Chem. Abstr.* 1981, 95, 24233.
- (443) Kuznetsov, O. I.; Panchenkov, G. M.; Tolkscheva, F. I. *Nef-tekhimiya* 1981, 21, 849.
- (444) Japanese Kokai 77 113 903, 1977; *Chem. Abstr.* 1978, 88, 120589d.
- (445) Beach, D. L.; Harrison, J. J. U.S. Patent 4 711 969, 1987; *Chem. Abstr.* 1988, 108, 77632p.
- (446) Page, N. M.; Young, L. B. U.S. Patent 4 855 527, 1989; *Chem. Abstr.* 1989, 111, 40133n.
- (447) Binger, P.; Brinkmann, A.; McMeeking, J. *Liebigs Ann. Chem.* 1977, 1065. Binger, P.; McMeeking, J. *Angew. Chem.* 1973, 85, 1053; *Angew. Chem., Int. Ed. Engl.* 1973, 12, 995.