



“NOVEL CATALYST SYSTEMS BASED ON Ni(II), Ti(IV) AND Cr(III)  
COMPLEXES FOR OLIGO - AND POLYMERIZATION OF ETHYLENE”

*FERNANDO JUNGES*

Thesis for the obtention of Ph. D. Degree

Prof. Dr. Osvaldo de Lázaro Casagrande Jr.

Adviser

Porto Alegre

September 2005

# **Livros Grátis**

<http://www.livrosgratis.com.br>

Milhares de livros grátis para download.

### 1. PERSONAL DATA

Name: Fernando Junges

Parents: Mário José Junges and Estela Maria Helm Junges

Born: 07/02/1976, Porto Alegre/RS - Brazil

Identity: 1056531153

CPF: 921613240-04

Residential Address: Rua Sapé, 105 - 257

Passo D'Areia

91350-050 Porto Alegre, RS - Brazil

Phone: (+55)(51)92541568

E-mail: [fjunges@iq.ufrgs.br](mailto:fjunges@iq.ufrgs.br)

Professional Address: K-208B Laboratory, Chemistry Institute, Campus do Vale

Federal University of Rio Grande do Sul

Av. Bento Gonçalves, 9500, Agronomia,

91501-970, Porto Alegre, RS – Brazil

Phone: (+55)(51)33167210

## 2. EDUCATION

2001 – 2005 Chemistry Ph.D.

Federal University of Rio Grande do Sul (UFRGS), Chemistry Institute, Porto Alegre, Rio Grande do Sul, Brazil.

Title: “Novel Catalyst Systems Based on Ni(II), Ti(IV) and Cr(III) Complexes for Oligo- and Polymerization of Ethylene”

Year: 2002

Mastermind: Osvaldo de Lazaro Casagrande Jr.

Fellowship: Conselho Nacional de Desenvolvimento Científico e Tecnológico, CAPES.

2001 Student (entrance)

Federal University of Rio Grande do Sul (UFRGS), Chemistry Institute, Porto Alegre, Rio Grande do Sul, Brazil.

Title: “Ni( $\alpha$ -diimine)Cl<sub>2</sub> ( $\alpha$ -diimine = 1,4-bis(2,6diisopropylphenil)-acenaphetodiimine Immobilized in Inorganic Supports and Applied in the Ethylene Polymerization”

Year: 2001

Mastermind: Osvaldo de Lazaro Casagrande Jr.

2002 Direct transposition to Ph.D. student.

1995 – 2000 Graduated School – Bachelor in Chemistry Degree

Federal University of Rio Grande do Sul (UFRGS), Chemistry Institute, Porto Alegre, Rio Grande do Sul, Brazil.

## EXAMINING COMMISSION

---

- Osvaldo de Lázaro Casagrande Júnior (mastermind) –Professor at the University Federal of Rio Grande do Sul, Chemistry Institute, Porto Alegre, Rio Grande do Sul, Brazil.
- Jean-François Carpentier (mastermind) – Professor at the Rennes-1 University, Chemistry Institute, Rennes, Bretagne, France.
- Márcia L. Miranda – Researcher at BRASKEM, Triunfo, Rio Grande do Sul, Brazil.
- Luiz A. Pessan – Professor at University Federal of São Carlos, Department of Materials Science and Engineering, São Carlos, São Paulo, Brazil.
- Michèle O. de Souza - Professor at the University Federal of Rio Grande do Sul, Chemistry Institute, Porto Alegre, Rio Grande do Sul, Brazil.
- Roberto F. de Souza - Professor at the University Federal of Rio Grande do Sul, Chemistry Institute, Porto Alegre, Rio Grande do Sul, Brazil.
- Griselda Galland - Professor at the University Federal of Rio Grande do Sul, Chemistry Institute, Porto Alegre, Rio Grande do Sul, Brazil.

## GRATEFULNESS

---

- To my parents Mário and Estela by the incentive, inspiration, love and affection.
- To Tatiana Nichele for being present in every moment.
- To Prof. Dr. Osvaldo of Lázaro Casagrande Jr. for the orientation of this work and for the granted opportunity, and more than this, for the friendship, trust, understanding and dedication demonstrated.
- To Prof. Dr. Jean-François Carpentier for receive me in his laboratory and orientation.
- To Dr. Jairton Dupont and Dr. João Henrique dos Santos, for the incentive, for the dedication and for the disposition to the directness in any moment.
- To Dr. Márcia L. Miranda, to Prof. Dr. Luiz A. Pessan, to Prof. Dr. Michèle O. de Souza, to Prof. Dr. Roberto F. de Souza and to Prof. Dr. Griselda Galland, for the participation in the examining commission.
- To CAPES and CNPQ for the financial support.
- To the Institute of Chemistry of UFRGS, where the experimental development was accomplished.
- To the friends Lobo, Elton, Fábio Kunrath, Fábio Mota, Luciano, Maria Cristina, Andressa, Patricia, Mariana, Gorga, Cláudia and other colleagues of the Institute of Chemistry (UFRGS), for many “helps”, for the friendship and for the company during this work.
- To the friends Emilio, Dante, Christoph and Mattew, to the colleagues Nourredine, Abder, Laurent, Simona, Anne-Sophia and Christoph Thomas that I knew in Rennes, for the numerous helps.
- To the friends of AEQ, Shirley, Fabi, Aline, Dove, Natacha, Eichler, Vander and principally the professor Del Pino for the innumerous “coffees” and conversation.
- To the soccer friends, for the moments of tension and stress release.

CURRICULUM DATA .....	II
EXAMINING COMMISSION .....	IV
GRATEFULNESS .....	V
FIGURES INDEX.....	IX
TABLES INDEX .....	XIII
ABBREVIATIONS.....	XIV
SCIENTIFIC PRODUCTION ORIGINATING FROM THIS THESIS .....	XVI
ABSTRACT .....	XVII
RÉSUMÉ.....	XX
I. INTRODUCTION.....	1
II. BIBLIOGRAPHIC REVISION .....	4
II.1 GENERAL ASPECTS .....	5
II.2 CATALYTIC SYSTEMS BASED ON NICKEL/ $\alpha$ -DIMINE COMPLEXES FOR OLEFIN POLYMERIZATION .....	9
II.2.1 <i>Nickel/<math>\alpha</math>-diimine complexes in homogeneous processes</i> .....	9
II.3 SUPPORTS FOR HETEROGENEOUS CATALYSTS.....	13
II.3.2 <i>Nickel/<math>\alpha</math>-diimine complexes in heterogeneous processes</i> .....	20
II.4 POLYMER BLENDS .....	24
II.4.1 <i>General Aspects</i> .....	24
II.4.2 <i>Preparation methods</i> .....	25
II.5 THE IN SITU IMPREGNATION OF HETEROGENEOUS CATALYSTS.....	27
II.6 OLEFIN OLIGOMERIZATION PROCESSES .....	30
II.6.1 <i>General Aspects</i> .....	30

II.6.2	<i>The discovery of the ethylene trimerization</i> .....	31
II.6.3	<i>Homogeneous trimerization catalysts based on chromium</i> .....	32
II.6.4	<i>Mechanistic considerations and molecular modelling</i> .....	45
III.	EXPERIMENTAL .....	50
III.1	General Procedures .....	51
III.2	Preparation of the supported Catalysts.....	51
III.2.1	<i>Preparation of SiO<sub>2</sub>/MAO (4.0 and 8.0 wt.-% Al/SiO<sub>2</sub>)</i> .....	51
III.2.2	<i>General procedure for preparation of Ni(II) supported catalysts</i> .....	52
III.3	Synthesis of Chromium compounds .....	52
III.3.1	<i>Syntheses of Ligands</i> .....	52
III.3.2	<i>Complexes of Cr (III):</i> .....	56
III.4	Characterization of the supported catalysts.....	59
III.4.1	<i>X-Ray Fluorescence Spectroscopy</i> .....	59
III.5	Polymerization reactions .....	59
III.6	Characterization of the polymers and oligomers.....	61
III.6.1	<i>Differential Scanning Calorimetry</i> .....	61
III.6.2	<i>Gel Permeation Chromatography</i> .....	61
III.6.3	<i>Nuclear Magnetic Resonance</i> .....	63
III.6.4	<i>Intrinsic Viscosities</i> .....	63
III.6.5	<i>Scanning Electronic Microscopy</i> .....	63
III.6.6	<i>Gas Chromatographic Analysis</i> .....	63
IV.	RESULTS AND DISCUSSION .....	64
IV.1	Ni( $\alpha$ -diimine)Cl <sub>2</sub> SUPPORTED ON MAO-MODIFIED SILICA: INFLUENCE OF POLYMERIZATION PARAMETERS ON ACTIVITY AND POLYMER PROPERTIES	



IV.1.1	<i>Preparation of the supported catalysts</i> .....	66
IV.1.2	<i>Ethylene polymerization using the supported catalysts S1-S4</i> .....	68
IV.1.3	<i>Effects of the polymerization conditions using the supported catalyst S2</i> .....	71
IV.1.4	<i>"In situ" heterogeneization of NiDADCl<sub>2</sub> on MAO-modified silica</i> .....	79
IV.2	ETHYLENE POLYMERIZATION USING COMBINED Ni AND Ti CATALYSTS SUPPORTED IN SITU ON MAO-MODIFIED SILICA .....	81
IV.2.1	<i>Influence of <math>x_{Ni}</math> and polymerization temperature on catalyst activity</i> .....	82
IV.2.2	<i>Influence of <math>x_{Ni}</math> and polymerization temperature on the polymer properties</i> ...	86
IV.2.3	<i>Morphology studies</i> .....	88
IV.3	SYNTHESIS, CHARACTERIZATION Of Cr <sup>III</sup> COMPOUNDS HAVING TRIDENTATE LIGANDS AND THEIR USE IN ETHYLENE OLIGOMERIZATION REACTIONS .....	91
IV.3.1	<i>General Aspects</i> .....	91
IV.3.2	<i>Synthesis and characterization of Cr<sup>III</sup> complexes</i> .....	91
IV.3.3	<i>Oligomerization of ethylene</i> .....	98
V.	CONCLUSIONS.....	107
VI.	REFERENCES.....	110

## FIGURES INDEX

---

Figure II.1: PE overview.....	6
Figure II.2: Representation of scope of the challenge for a new material today.....	7
Figure II.3: Evolution of polyethylene structure.....	9
Figure II.4: General structure of the Brookhart complex.....	11
Figure II.5: Mechanism of ethylene polymerization in the presence of nickel-diimine complexes. <sup>12</sup> .....	12
Figure II.6: Structural schemes of various OH sites found at the hydrated amorphous silica surface.....	14
Figure II.7: Schematic representation of the dehydration of a silica gel surface. <sup>19</sup> .....	15
Figure II.8. Structure of the MAO.....	17
Figure II.9. Representation of the immobilization of the complex tris(pyrazolyl)borate imido vanadium to the MAO-modified silica.....	19
Figure II.10: Structures of the complexes Ni( $\alpha$ -diimine) of Brookhart.....	22
Figure II.11. Synthesis of Supported Complex 2.....	22
Figure II.12: Structure of the complexes of Brookhart.....	23
Figure II.13. Structure of the catalyst $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ .....	28
Figure II.14. Trimerization of ethylene made with Cr(III) 2-EH and the ligand 5-(4- <i>t</i> -butylphenyl)-1,2,3,4-tetraphenylcyclopentadienyl activated by TEA.....	34
Figure II.15. Trimerization of ethylene made with [1,4,7-trimethyl-1,4,7-triazacyclononane]CrCl <sub>3</sub> activated by NHAO.....	37
Figure II.16. Trimerization of ethylene made with tris(3,5-dimethyl-1-pyrazolyl)methane chromium trichloride activated by MAO.....	38

Figure II.17. Trimerization of ethylene made with (2-dimethylphosphinoethyl)(3-dimethylphosphinopropyl) phenylphosphine chromium trichloride activated by BuAO.	39
Figure II.18. Trimerization of ethylene made with $\text{CrCl}_3(\text{THF})_3$ and (2-methoxyphenyl) $_2$ PN(Me)P(2-methoxyphenyl) $_2$ activated by MAO.	40
Figure II.19. Synthesis of Cr(III) complexes with the ligand bis-phosphinoamine ( $\text{R}_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{PR}_2$ ).	41
Figure II.20. Trimerization of ethylene made with [bis-(2-diethylphosphinoethyl)amine] $\text{CrCl}_3$ activated by MAO.	42
Figure II.21. Synthesis of Cr(III) complexes with the SNS ligand bis-(2-alkylsulphanyl-ethyl)-amine.	43
Figure II.22. Trimerization of ethylene made with [bis-(2-decylsulphanyl-ethyl)-amine] $\text{CrCl}_3$ activated by MAO.	43
Figure II.23. Trimerization of ethylene made with PNP imine complex of Cr activated by MAO.	44
Figure II.24. Trimerization of ethylene made with PNS imine complex of Cr activated by MAO.	45
Figure II.25. Mechanism of formation of linear alpha olefins proposed by Cossee and Arlman. <sup>88</sup>	46
Figure II.26. Mechanism of trimerization of ethylene metallocycle-based proposed by Manyik et al. <sup>65</sup>	47
Figure II.27. Mechanism of trimerization of ethylene for the Phillips $\text{CrO}_3/\text{SiO}_2$ catalyst proposed by Briggs. <sup>90</sup>	48
Figure II.28. Mechanism of trimerization of ethylene for the tetrahedral $\text{CrO}_3\text{Si}_2\text{H}_4$ mononuclear cluster, here only partially reproduced as a -O-Cr-O- fragment of the ring. <sup>95,96</sup>	49

Figure III.1. Reactors used in the polymerization reactions. ....	62
Figure IV.1 Correlation between nature of the support and Ni content (wt.%). ....	67
Figure IV.2. Correlation between the activity, wt.% Al/SiO <sub>2</sub> and the $\chi_{Ni}$ immobilized in the silica modified with MAO in the polymerization reactions for 30°C, in toluene and using a molar ratio Al/Ni = 1000. ....	69
Figure IV.3. Effect of the ratio Al/Ni about the catalytic activity for the system S2. ....	73
Figure IV.4. Effect of the temperature in the catalytic activity of the system S2. ....	74
Figure IV.5. DSC curves of polymers using the catalytic precursors 1 and S2. Polymerization Conditions: reactor of steel inox (75 mL); pressure of ethylene of 30 atm, ratio [Al]/[Ni] = 1000 at 60°C for 5 minutes. ....	77
Figure IV.6. Polyethylene produced using 1 (a) and S2 (b) (60°C, 30 atm, toluene, [Al]/[Ni] = 1000). ....	77
Figure IV.7. Influence of polymerization temperature on the activity for 1/2/S2 varying $x_{Ni}$ . ....	85
Figure IV.8. DSC thermograms of the polyethylenes produced by 2/1/S2 at 0°C. ....	87
Figure IV.9. Influence of the immobilization order and $x_{Ni}$ on the melting temperature of the polyethylene blends produced at 0°C. ....	88
Figure IV.10. SEM micrographs of BPE/HDPE blends crio-fractured surfaces produced by 2/1/S2 at 0 °C: (a) $x_{Ni}$ = 0.50; (b) $x_{Ni}$ = 0.50 after etched with o-xylene at 80 °C. ....	90
Figure IV.11. SEM micrographs: (a) 2/1/S2 ( $x_{Ni}$ = 0.50, 1500 x); (b) polyethylene blend produced by 2/1/S2 at 0°C ( $x_{Ni}$ = 0.50, 1500 x). ....	90
Figure IV.12. Synthesis of the Cr <sup>III</sup> catalysts 3a-d. ....	92
Figure IV.13. Structures of the Cr <sup>III</sup> catalysts 3a-d. ....	92
Figure IV.14. Molecular structure of compound 3c (the hydrogen atoms was omitted for clarity). ....	94

Figure IV.15. Turnover frequency (TOF) varying the Cr <sup>III</sup> catalyst (ethylene oligomerization reaction performed at 80°C under ethylene pressure of 20 atm, and using 30 μmol of catalyst). .....	99
Figure IV.16. Selectivity (%) for olefin total varying the Cr <sup>III</sup> catalyst (ethylene oligomerization reaction performed at 80°C under ethylene pressure of 20 atm, and using 30 μmol of catalyst). .....	101
Figure IV.17. Selectivity (%) for α-olefin varying the Cr <sup>III</sup> catalyst (ethylene oligomerization reaction performed at 80°C under ethylene pressure of 20 atm, and using 30 μmol of catalyst). .....	102
Figure IV.18. Mass of α-olefin produced varying the Cr <sup>III</sup> catalyst (ethylene oligomerization reaction performed at 80°C under ethylene pressure of 20 atm, and using 30 μmol of catalyst). .....	103
Figure IV.19. DSC curves of the polyethylenes produced by 3a at 80°C varying the ethylene, and using 30 μmol of catalyst). .....	104
Figure IV.20. Effect of temperature on the selectivity using 3d. ....	105
Figure IV.21. Effect of the ethylene pressure on the selectivity using 3c. ....	106

Table IV.1 Resulting Ni content in the supported catalysts.....	67
Table IV.2: Ethylene polymerization, using the catalytic precursor 1 immobilized in silica and MAO-modified silica. <sup>a</sup> .....	68
Table IV.3. Ethylene polymerization using S2. <sup>a</sup> .....	71
Table IV.4. Results of ethylene polymerization at high pressures using the catalytic precursors 1 and S2. <sup>a</sup> .....	76
Table IV.5. Ethylene polymerizations with different cocatalyst using the system S2. <sup>a</sup> .....	78
Table IV.6. Ethylene polymerization results using Ni(diimine- $\alpha$ )Cl <sub>2</sub> (1) catalyst supported <i>in situ</i> on S2. <sup>a</sup> .....	80
Table IV.7. Ethylene polymerization results using combined Ni(diimine- $\alpha$ )Cl <sub>2</sub> (1) and {Tp <sup>M<sub>s</sub>*</sup> }TiCl <sub>3</sub> (2) catalysts supported <i>in situ</i> on S2. <sup>a</sup> .....	84
Table IV.8. Summary of Crystallographic Data for the complex 3c. ....	95
Table IV.9. Atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ). ( $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.).....	96
Table IV.10. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ].....	97
Table IV.11. Results of reactions of Oligomerization/Polymerization of ethylene.....	100

## ABBREVIATIONS

---

AlR <sub>3</sub>	= trialkylaluminum
Cp	= cyclopentadienyl
DAD	= 1,4-bis(2,6-diisopropylphenyl)-acenaftenodiimine
DME	= dimethoxymethane
DRIFTS	= diffuse reflectance infra-red fourier transform
DSC	= differential scanning calorimetry
EPMA	= electron probe microanalyze
FT-IR spectroscopy	= fourier transform-infra red spectroscopy
GPC	= gel permeation chromatography
HDPE	= high-density polyethylene
Ind	= indenyl
IPRA	= isopropylaluminium
LAO	= linear alpha olefins
LCB-PE	= long chain branches polyethylene
LDPE	= low density polyethylene
LLDPE	= linear low-density polyethylene
LPE	= linear polyethylene
MAO	= methylaluminoxane
M <sub>w</sub>	= molecular weight
M <sub>w</sub> D	= polydispersity
PE	= polyethylene
PIBAO	= tri-isobutylaluminium partially hydrolyzed

SEM	= scanning electron microscopy
<i>t</i> -Bu	= terc-buthyl
TEA	= triethylaluminium
TiBA	= tri-isobuthylaluminium
T <sub>m</sub>	= melt transition
TMA	= trimethylaluminium
TOF	= turnover frequency
TpMs <sup>*</sup>	= tris[(3-mesitilpyrazolil) <sub>2</sub> (5-mesitilpyrazolil)]borate
XRF	= X-ray fluorescence spectroscopy



**1. Complete papers published in journals.**

Junges, F.; de Souza, R.F.; dos Santos, J.H.Z.; Casagrande, O.L.; “Ethylene polymerization using combined Ni and Ti catalysts supported in situ on MAO-modified silica.” *Macromolecular Materials and Engineering* **2005**, 290 (1), 72.

**2. Complete works published in event historical records**

Junges, F.; Casagrande, O.L.; de Souza, R.F.; dos Santos, J.H.Z.; Mauller, R.S.; Marcico, P.D.; “Ni(II)-Diimina Suportado sobre MgCl<sub>2</sub> Aplicado na Polimerização do Etileno”. In 11° Congresso Brasileiro de Catálise e 1° Congresso de Catálise do Mercosul, 2001, Bento Gonçalves – RS.

Junges, F.; dos Santos, J.H.Z.; de Souza, R.F.; Casagrande, O.L.; “Polimerização do etileno por Ni(diimina- $\alpha$ )Cl<sub>2</sub> imobilizado em sílicas modificadas com metilaluminoxano”. In 12° Congresso Brasileiro de Catálise, 2003, Angra dos Reis – RJ.

The complex of Brookhart  $\text{Ni}(\alpha\text{-diimine})\text{Cl}_2$  (**1**) ( $\alpha\text{-diimine}$  = 1,4-bis(2,6-diisopropylphenyl)-acenaphthenediimine) has been characterized after impregnation on silica (**S1**) and MAO-modified silicas (4.0, 8.0 and 23.0 wts.% Al/SiO<sub>2</sub> called **S2**, **S3** and **S4**, respectively). The treatment of these heterogeneous systems with MAO produces some active catalysts for the polymerization of the ethylene. A high catalytic activity has been gotten while using the system supported **1/S3** (196 kg of PE/mol[Ni].h.atm; toluene, Al/Ni = 1000, 30°C, 60 min and atmospheric pressure of ethylene). The effects of polymerization conditions have been tested with the catalyst supported in **S2** and the best catalytic activity has been gotten with solvent hexane, MAO as cocatalyst, molar ratio Al/Ni of 1000 and to the temperature of 30°C (285 kg of PE/mol[Ni].h.atm). When the reaction has been driven according to the *in situ* methodology, the activity practically doubled and polymers showed some similar properties. Polymers products by the supported catalysts showed the absence of melting fusion, results similar to those gotten with the homogeneous systems by DSC analysis. But then, polymers gotten with the transplanted system present according to the GPC's curves the polydispersity (MwD) varies between 1.7 and 7.0.

A polyethylene blend (BPE/LPE) was prepared using the complex  $\text{Ni}(\alpha\text{-diimine})\text{Cl}_2$  (**1**) ( $\alpha\text{-diimine}$  = 1,4-bis(2,6-diisopropylphenyl)-acenaphthenediimine) and  $\{\text{TpMs}^*\}\text{TiCl}_3$  (**2**) (TpMs\* = hydridobis(3-mesitylpyrazol-1-yl)(5-mesitylpyrazol-1-yl)) supported *in situ* on MAO-modified silica (4.0 wts. -% Al/SiO<sub>2</sub>, **S2**). Reactions of polymerization of ethylene have been executed in the toluene in two different temperatures (0 and 30°C), varying the molar fraction of nickel ( $x_{\text{Ni}}$ ), and using MAO as external cocatalyst. To all temperatures, the activities show a linear variation tendency with  $x_{\text{Ni}}$  and indicate the absence of the effect synergic between the species of nickel and the titanium. The maximum of activity have been

found at 0°C. The melting temperature for the blends of polyethylene produced at 0 °C decrease whereas  $x_{Ni}$  increases indicating a good compatibility between phases of the polyethylene gotten with the two catalysts. The melting temperature for the blends of polyethylene showed be depend on the order according to which catalysts have been supported on the MAO-modified silica. The initial immobilization of **1** on the support (**2/1/S2**) product of polymers with a melting temperature ( $T_m$ ) lower to the one of the polymer gotten when the titanium has been supported initially (**1/2/S2**). The observation of polyethylenes gotten with the two systems (**2/1/S2** and **1/2/S2**) by scanning electron microscopy (SEM) showed the spherical polymer formation showing that the spherical morphology of the support to been reproduced.

Are described the synthesis, the characterization and the catalytic properties for the oligomerization of the ethylene of four organometallics compounds of  $Cr^{III}$  with ligands ([bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine] chromium (III) chloride (**3a**), [bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]benzylamine] chromium (III) chloride (**3b**), [bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether] chromiun(III)chloride (**3c**), [bis[2-(3-phenyl-1-pyrazolyl)ethyl]ether]chromiun(III)chloride (**3d**)). In relation of the oligomerization, at exception made of the compounds **3a**, all complex of the chromium showed be active after activation with MAO and the TOF gotten have one effect differentiated to those formed with  $CrCl_3(thf)_3$ . The coordination of a tridentate ligand on the metallic center doesn't provoke any considerable changes on the formation of the  $C_4$  and  $C_6$ , but the amount of  $C_8$  are decrease and the  $C_{10}$  and  $C_{12+}$  have increased. The Polymers produced by the catalyst **3a** to 3 and 20 bar of ethylene have, according to analyses by DSC, the temperatures of fusion of 133,8 and 136°C respectively. It indicates that in the two cases the production of high density polyethylene. The molar mass, gotten by GPC, is 46647 g/mols with  $M_wD = 2,4$  (3 bar). The system **3c**/MAO showed values of TOF, activity and selectivity to different  $\alpha$ -olefins

according to the pressure of ethylene uses. Himself that shown a big sensibility to the concentration of ethylene solubilized.

Le complexe de Brookhart  $\text{Ni}(\alpha\text{-diimine})\text{Cl}_2$  (**1**) ( $\alpha\text{-diimine}$  = 1,4-bis(2,6-diisopropylphenyl)-acenaphthenediimine) a été caractérisé après impregnation sur silice (**S1**) et a silices modifié avec MAO (4,0, 8,0 et 23,0 wt.% Al/SiO<sub>2</sub> appelé **S2**, **S3** et **S4**, respectivement). Le traitement de ces composés greffé avec MAO produit des catalyseurs actifs pour la polymérisation de l'éthylène. Une haute activité catalytique a été obtenue en utilisant le système supporté **1/S3** (196 kg de PE/mol[Ni].h.atm; toluène, Al/Ni = 1000, 30°C, 60 min et pression atmosphérique d'éthylène). Les effets des conditions de la polymérisation ont été testés avec le catalyseur greffé **S2** et la meilleure activité catalytique a été obtenue avec le solvant hexane, MAO comme cocatalyseur, la proportion molaire Al/Ni de 1000 et à la température de 30°C (285 kg de PE/mol[Ni].h.atm). Quand la réaction a été conduite selon la méthodologie *in situ*, l'activité a pratiquement doublé et les polymères ont montré des propriétés semblables. Les polymères produits par les catalyseurs supportés ont montré l'absence de température de fusion, résultats semblables à ceux obtenus avec les systèmes homogène par analyse DSC. En revanche, les polymères obtenus avec le système greffé présentent selon les courbes GPC une (MwD) polydispersité qui varie de 1,7 à 7,0.

Un mélange de polyéthylène linéaire et ramifié (BPE/LPE) préparé utilisant les complexes  $\text{Ni}(\alpha\text{-diimine})\text{Cl}_2$  (**1**) ( $\alpha\text{-diimine}$  = 1,4-bis(2,6-diisopropylphenyl)-acenaphthenediimine) et  $\{\text{Tp}^{\text{Ms}^*}\}\text{TiCl}_3$  (**2**) ( $\text{Tp}^{\text{Ms}^*}$  = hydridobis(3-mesitylpyrazol-1-yl)(5-mesitylpyrazol-1-yl)) greffés *in situ* sur silice modifiée avec MAO (4,0 wt.-% Al/SiO<sub>2</sub>, **S2**). Les réactions de polymérisation ont été exécutées dans le toluène à deux températures différentes (0 et 30°C), variant la fraction molaire du nickel ( $x_{\text{Ni}}$ ), et utilisant MAO comme cocatalyseur externe. À toutes les températures, les activités montrent une tendance de variation linéaire avec  $x_{\text{Ni}}$  et indiquent l'absence d'effet synerque entre les espèces de nickel

et du titane. Des activités les plus élevées ont été trouvées à 0°C. Les températures de fusion pour les mélanges de polyéthylène produits à 0 °C diminuent alors que  $x_{Ni}$  augmente l'indiquant une bonne compatibilité entre les phases du polyéthylène obtenues avec les deux catalyseurs. La température de fusion des mélanges de polyéthylène dépendre de l'ordre selon lequel les catalyseurs ont été greffés sur la silice modifiée avec MAO. L'immobilisation initiale de **1** sur le support (**2/1/S2**) produit des polymères avec une température de fusion ( $T_m$ ) inférieure à celle des polymère obtenus lorsque le titane a été greffé initialement **1/2/S2**. L'observation des polyéthylènes obtenus avec les deux systèmes (**2/1/S2** et **1/2/S2**) par microscopie électronique à balayage (SEM) a montré la formation de polymère sphérique montrant que la morphologie sphérique du support a été reproduite.

Sont décrits la synthèse, la caractérisation et les propriétés catalytique pour l'oligomérisation de l'éthylène de quatre composés organometalliques du  $Cr^{III}$  possédante les ligands ([bis[2-(3,5-diméthyl-1-pyrazolyl)éthyl]amine]chromium(III)chloride (**3a**), [bis[2-(3,5-diméthyl-1-pyrazolyl)éthyl] benzylamine]chromium(III)chloride (**3b**), [bis[2-(3,5-diméthyl-1-pyrazolyl)éthyl]ether] chromium(III)chloride (**3c**), [bis[2-(3-phenyl-1-pyrazolyl)éthyl]ether]chromium(III)chloride (**3d**)). Concernent l'oligomérisation, exception faite du composé **3a**, tous les complexe du chrome se sont montré actif après activation avec MAO et les FR obtenues ont une effet différentiel à celles atteintes avec  $CrCl_3(thf)_3$ . La coordination d'un ligand tridentatè sur le centre métallique ne provoque pas de changements considérables sur la formation des  $C_4$  et  $C_6$ , mais la montante de  $C_8$  est diminuée et celles des  $C_{10}$  et  $+C_{12}$  ont été augmentées. Les polymères produits par le catalyseur **3a** à 3 et 20 atm d'éthylène possèdent, selon les analyses par DSC la températures de fusion de 133,8 et 136°C respectivement. Ceci indique que dans les deux cas la production de polyéthylène de haut densité. Effectivement le masse molar moyenne, obtenus par GPC, est de 46647 g/mol avec  $M_w/M_n = 2,4$  (3 atm). Le système **3c**/MAO a montré des valeurs de FR, activité et sélectivité

à  $\alpha$ -olefins différents selon la pression d'éthylène utilisée. Se qui montré une grand sensibilité à la concentration d'éthylène solubilisé.

## **I. INTRODUCTION**

---



The plastics represent one of most important market of chemical products in the world. In this reality, the development of different polyolefins occupies an important part of that market and it comes being very important to produce materials with properties and characteristics more specifics. To the polyethylene, the researches for new materials are basing on 3 great areas that are the production of new class of catalysts, the heterogeneization of the homogeneous catalysts and the mixture of known catalysts, to create blends.

Industrially, the production of polyethylene is based on the heterogeneous catalysts, such as: (i) Phillips type catalysts, (ii) Ziegler-Natta catalysts and (iii) single-site homogeneous catalysts or supported homogeneous catalysts; with this, comes being searched for the best reaction conditions to support catalysts, known for possess high activities in a phase homogeneous, in order to they be used in production plants.

Considering the necessity to adapt the homogeneous catalysts to the existent industrial technology, through the process of heterogeneization, we decided to carry out the immobilization of  $\text{NiCl}_2\text{DAD}$  (**1**) catalyst in silica and MAO-modified silica and investigate his performance in ethylene polymerization varying some polymerization parameters.

Considering that the complexes  $\text{NiCl}_2\text{DAD}$  (**1**) and  $\{\text{TpMs}^*\}\text{TiCl}_3$  (**2**) when used mixed in a polymerization reaction present an effect called “synergic effect” in homogeneous phase, what provokes an increase of the catalytic activity, being compared to the reaction of both separately, we decided to test if these effect is proven in heterogeneous phase. To make this study, the complexes were supported in silica modified with MAO and tested in polymerization of ethylene. The effect in the polymer properties was elucidating by CGP DSC and NMR.

Parallel to that study, it was also tested the ethylene polymerization using the combination of the complexes  $\text{NiCl}_2\text{DAD}$  (**1**) and  $\{\text{TpMs}^*\}\text{TiCl}_3$  (**2**) supported *in situ* on

silica modified with MAO. The influence of  $\chi_{Ni}$  and polymerization temperature on catalyst activity and the polymer morphology was tested.

The chromium complexes are very used industrially for the oligomerization (mainly millstone process of trimerization) of ethylene as the Phillips catalysts, we decided to investigate the influence of a new class of ligands tridentates actives in the polymerization, when linked to metals of transition of the groups IV, with the chromium. We started by the synthesis and characterization of these ligands and chromium complexes to later test in the polymerization of the ethylene.

## **II. BIBLIOGRAPHIC REVISION**

---

## II.1 GENERAL ASPECTS

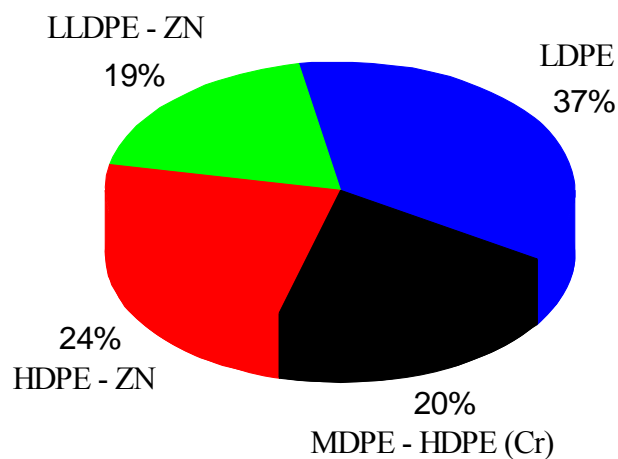
Every day, the plastics come being used more and more in the most differentiated areas of the society, presenting several usefulness and characteristics. The polymeric materials are used in the production of sacs, coatings, food processing (conveyor belt chains for high-speed beverage and food processing lines) and transportation (until recently, carbon fiber composites only appeared on concept cars or very high priced “super cars”) even in the most specific as in the medicine, or in the electronics, like the in-car fiber optic data network or the electronically communicating label.

After the discovery of olefin polymerization catalysts in the early 1950s by Ziegler and Natta, the industrial production of polyolefins presented a great evolution until the current days, as the fourth generation Ziegler-Natta catalysts and metallocene-based “single site” catalysts. These catalysts present activity and stereoselectivity close to those of enzymatic processes. The industrial processes work at low costs and are environmental friendly. When the polyethylenes (PEs) lost their performance, they can be recycled for energy production.<sup>1</sup> Three classes of olefin polymerization catalysts can be distinguished as follows: (i) Phillips type catalysts, which are composed of a chromium oxide supported on an amorphous material such as silica;<sup>2</sup> (ii) Ziegler-Natta catalysts, which consist of a transition metal compound and an activator ( $\text{AlR}_3$ , MAO, etc.) whose function is to introduce an alkyl group in the coordination sphere of the metal;<sup>3</sup> and (iii) single-site homogeneous catalysts or supported homogeneous catalysts, like metallocene catalysts<sup>1,4</sup> and incompletely condensed silsesquioxane,<sup>5</sup> which also need an activator.

The production of polyolefins is nowadays a multibillion dollar industrial activity. The polyolefins represents 60% of the world demand of thermoplastics approximately, where the polyethylenes are inserted in the landing of the 40%. Annually more than 100 million

metric tons of polyolefins are produced. These processes use different conditions (Figure II.1) in high pressures, bulk or gas phase using autoclaves, tubular, loop or reactor types designed for gas polymerization, the world production of polyolefins can be represented in the Figure II.1, where catalyst Ziegler-Natta is responsible for 43% of production and the catalytic precursors based on Cr for 20%. Almost all processes require a catalytic system for the activation of the monomer, exceptionally for high pressures of ethylene and temperatures.

The field of olefin polymerization catalysis has experienced an acceleration in research activity over the past 10 years, with many academic and industrial research laboratories engaging in the design of coordination and organometallic precatalysts for the controlled synthesis of polyolefin products.<sup>6</sup>



**Figure II.1:** PE overview.

The development of the history of mankind is strictly linked to material and these really marked in the main steps or eras in that history. With more scientific and modern approach with respect to the past generations, we could say that one ideal material has to fulfill the new challenging and demanding needs of mankind, so the scope of the challenge for

a new material today, and more in the future, has to follow a very committing but unavoidable rule:

- Imagine the concept;
- Identify scientifically;
- Create industrially;
- Produce economically and with total respect for the environment.

We can see one representation of these characteristics in the Figure II.2:

IMAGINE	The building blocks of macromolecules, its basic structure and steric shape, the MW, MWD.
IDENTIFY SCIENTIFICALLY	The exploitation of the potential of the catalyst, variety range of usable monomer, chemical and physical retail ring, blending alloys, composite structuring.
CREATE INDUSTRIALLY	The possibility of creating single, versatile and low energy consumption processes and products.
MANUFACTURE ECONOMICALLY SEEKING TOTAL FRIENDLINESS	Maximize the performance/cost balance and minimize the impact on the environment unequalled (unmatchable) by any other family of the materials.

**Figure II.2:** Representation of scope of the challenge for a new material today.

The polyolefins were leveled with the poorest commodities. However, although “commodities” has been considered as the appropriate term to define polyolefins in their first 30 years; in the last 15 years, this has been protagonist of an excellent innovation process though a continuous development of new process and products.

The Brazilian market of polyolefins represents about 65%, of which 43% correspond to the polyethylenes and grows twice in a rhythm superior to the gross domestic product (GDP). Between 1999 and 2000, the sales increased in more than 150 thousand tons (about 10% of the national production) and the total market of polyethylenes in the country is 1.6 million tons and it has been growing to a reason of 5% a year. That rate means an increment of 80 thousand tons by year. Staying in this rhythm, in 2008 the production capacity has been reached, being necessary the amplification of the existent plants of polyethylene. The market of linear polyethylene moves strongly forward in relation to the conventional low density resin, whose sales are static and its production presents fall tendency.<sup>7</sup>

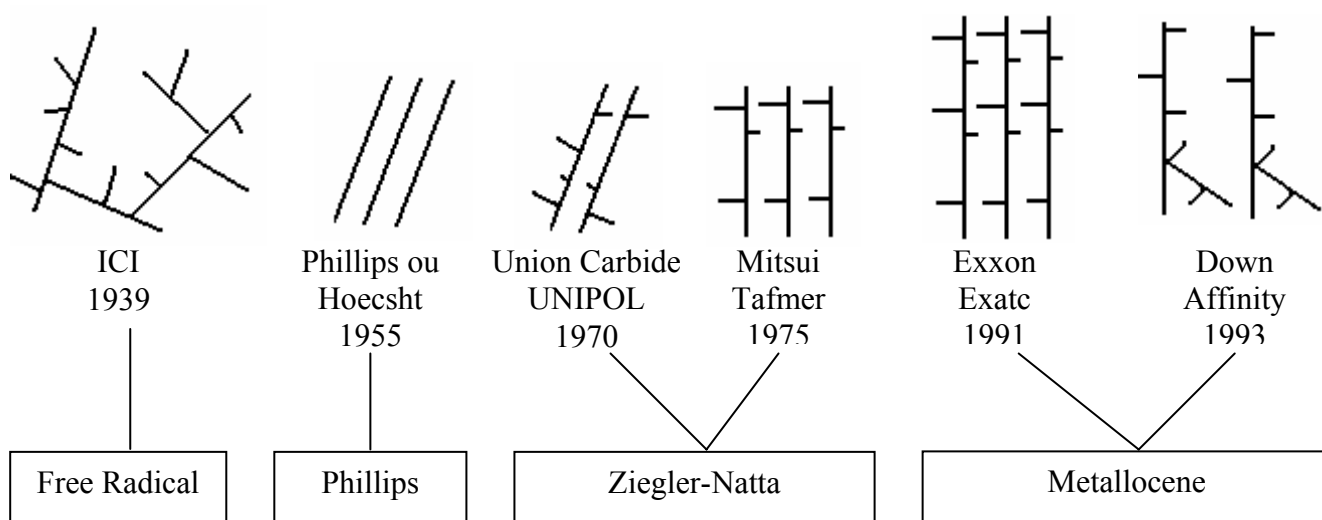
In this context, the search for new technologies for the polyolefins development has been intense in the last years. Besides, the heterogeneization of these new developed homogeneous catalysts is necessary taking into account that the most of the existent industrial plants use the heterogeneous catalysts.

## II.2 CATALYTIC SYSTEMS BASED ON NICKEL/ $\alpha$ -DIMINE COMPLEXES FOR OLEFIN POLYMERIZATION

### II.2.1 Nickel/ $\alpha$ -diimine complexes in homogeneous processes

The first polymerization process using high temperature and pressure was developed by ICI researchers in the 1930s. This process was commercialized in 1939 where ethylene is converted, via a radically initiated polymerization mechanism, to polyethylene chains having broad polydispersity (MwD) and a large number of side branches with different sizes. The branches are produced *in situ* according to the mechanism called “back-biting”. The low density polyethylene (LDPE) produced by this process has a density between 0.91 – 0.93 g/cm<sup>3</sup>.

The polyethylene structures produced by different types of catalyst can be summarized in Figure II.3.

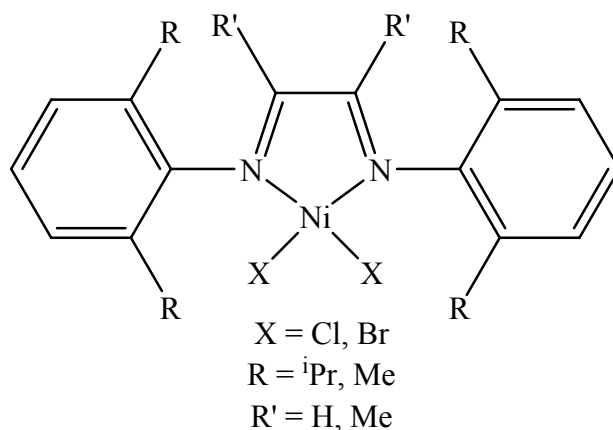


**Figure II.3:** Evolution of polyethylene structure<sup>8</sup>



Typical PE's produced by metallocene catalysts show MwD around 2.0 and from 0.9 to 1.2 methyl groups per 1000 carbon atoms. Bimodal MwD can be achieved by mixing of different types of catalysts. Furthermore, the molecular weight can be readily decreased either by increasing the temperature of polymerization, raising then metallocene/ethylene ratio or by adding small amounts of hydrogen in the polymerization medium.<sup>9</sup> Melting temperatures of these polymers are around 134 - 140°C, and the density increases after initial melt passing to 0.947 - 0.953 g/cm<sup>3</sup>.

Besides, the well-defined metallocene catalysts, during the first half of the 1990s, interest grew in developing new generation "non-metallocene" catalysts, partly to avoid the growing patent minefield in Group 4 cyclopentadienyl systems, but also to harness the potential of other metals to polymerize ethylene on its own and with other olefinic monomers. It was a discovery in the mid-1990s that was to have a galvanizing effect on researchers in the polyolefin catalysis field. Although some earlier work on nickel catalyst systems of the type employed in the Shell Higher Olefin Process (SHOP) had revealed the potential for late transition metals to polymerize ethylene, it was the discovery of highly active ( $\alpha$ -diimine) nickel catalysts (Figure II.4) capable of polymerizing ethylene to either linear or highly branched polyethylene (PE), depending on the ligand backbone and reaction conditions, that dramatically demonstrated the possibilities for expanding the commercially useful metals beyond the first half of the transition series.<sup>10</sup>

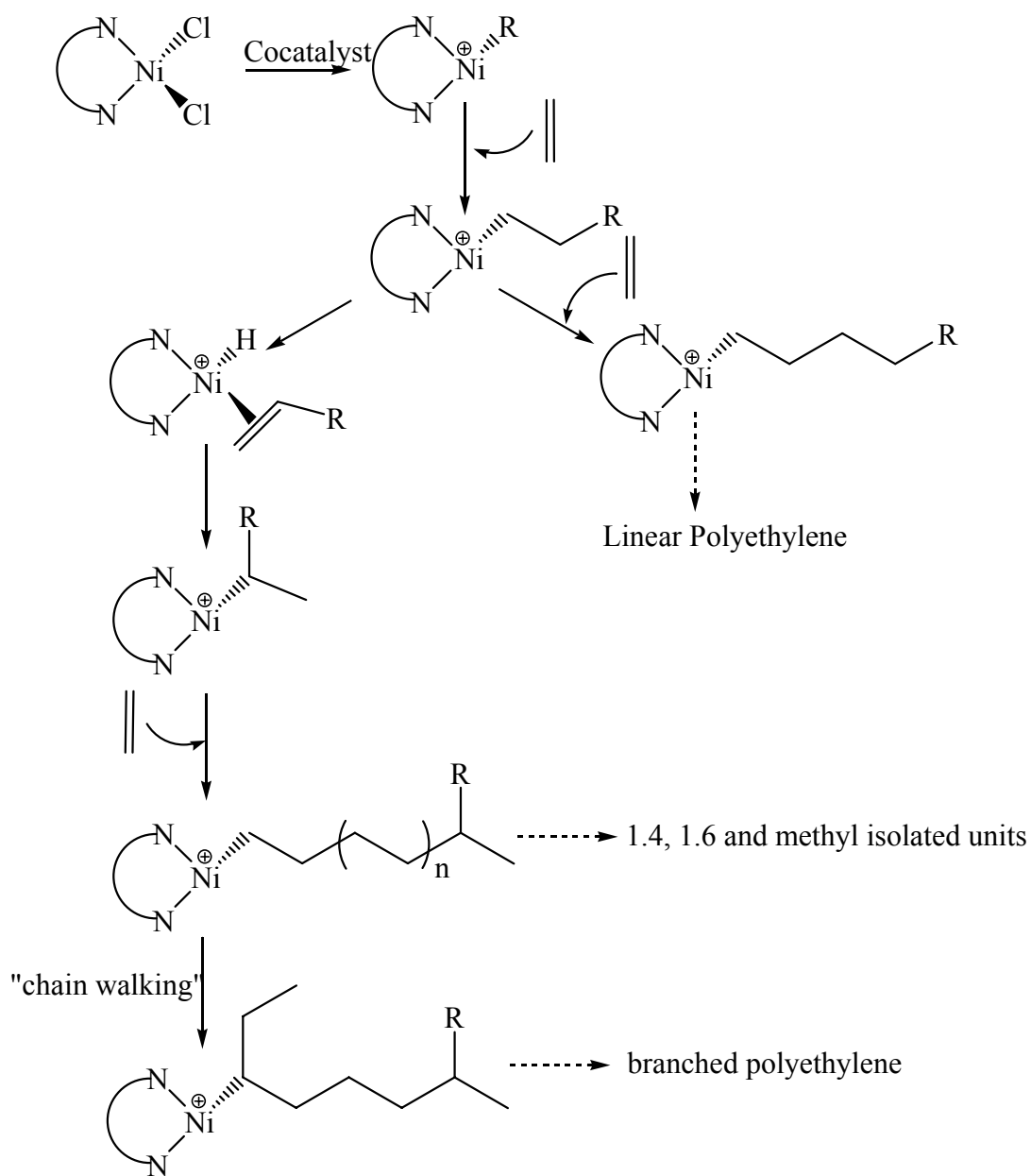


**Figure II.4:** General structure of the Brookhart complex.

Three key features of the original  $\alpha$ -diimine polymerization catalysts are (i) highly electrophilic, cationic nickel and palladium metal centers; (ii) the use of sterically bulky  $\alpha$ -diimine ligands; and (iii) the use of noncoordinating counterions or the use of reagents thought to produce noncoordinating counterions.<sup>11</sup>

The Brookhart's catalyst when activated with MAO in reaction at 25 °C shows activity of 11000 kg of PE/mol[Ni].h.atm. Besides the ethylene polymerization, this catalyst type is capable of polymerizes  $\alpha$ -olefins producing polymers with high molecular weight. This catalyst is able to produce polymers with an enormous variety of structures, from amorphous materials highly branched to linear ones, just for the simple variation of pressure, temperature or by modification of the groups presents in the ligands.

The selectivity in the distribution of methyl branches separated by one or two ethylene units and the formation of bimodal molecular weight distributions should be included in a mechanism that describes the ethylene polymerization in the presence of cationic nickel-diimine complexes. Figure II.5 shows a possible mechanism which explains the formation of linear and branched polyethylenes, as previously proposed by Okuda<sup>12</sup>, taking into account the “*chain walking*” process.



**Figure II.5:** Mechanism of ethylene polymerization in the presence of nickel-diimine complexes.<sup>12</sup>

### II.3 SUPPORTS FOR HETEROGENEOUS CATALYSTS

While these new Ni(II) catalysts show great performance in homogeneous medium, most of the existing polymerization plants run a slurry- and gas-phase process with heterogeneous catalysts, such homogeneous ones must be heterogeneized on a support for the application in those processes. Furthermore, the heterogeneization of catalysts is necessary to avoid reactor fouling with finely dispersed polymer crystals, to prevent excessive swelling of polymer, and to produce polymer particles of a desired regular morphology.

Several immobilization routes for homogeneous systems have been described in the literature, considering that the major of them is related to the heterogeneization of metallocene compounds.<sup>13</sup>

This process, normally, can be classified in three groups: (i) the direct impregnation of catalysts in the support; (ii) systems modified with MAO, and (iii) immobilization in supports chemically modified.

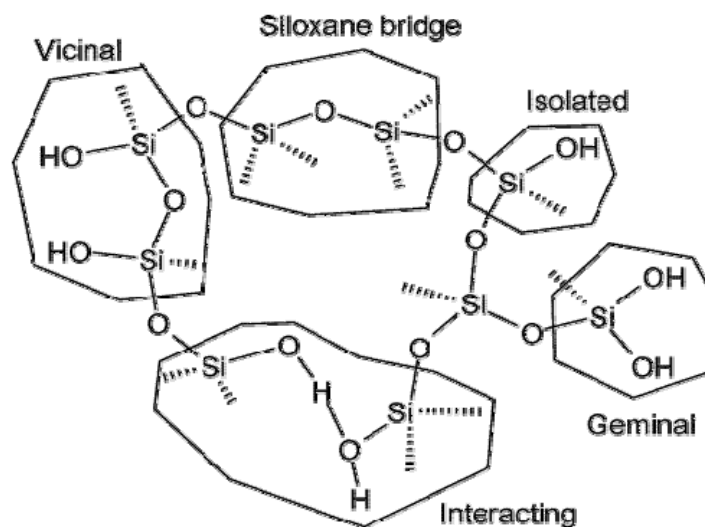
Several types of organic and inorganic supports such as silica, alumina, alumina-silicates (also called zeolites), composed of magnesium ( $MgCl_2$  and  $MgO$ ) and even the methylaluminoxane (MAO)<sup>14</sup> have been used in the immobilization of homogeneous catalysts, but the choice of those should be based on some aspects<sup>15</sup> such as:

- Specific area of the support;
- Access easy to the fixation ranches and;
- Stability in the conditions of polymerization.

Based on these aspects mentioned above, silica has been elected as a main inorganic support applied in the heterogeneization of soluble catalysts.

### II.3.1.1 Silica

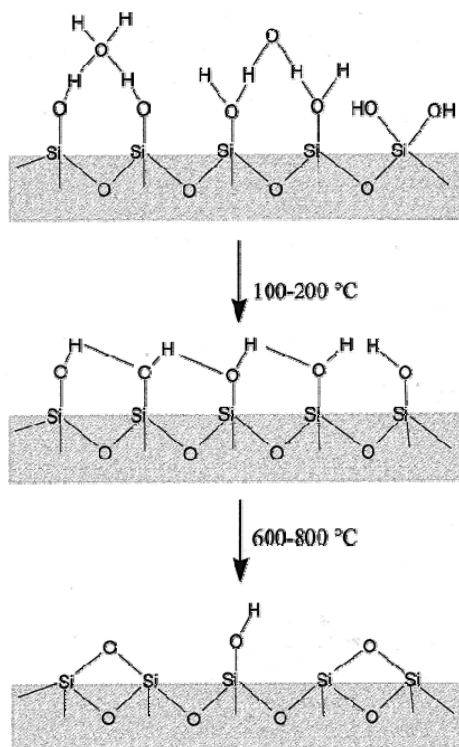
The chemical properties of amorphous silica are mostly governed by the chemistry of its surface, especially by the presence of silanols groups. In the surface of silica we can identify diverse functional groups, differing either by the number of hydroxyl groups per Si atom or by their spatial proximity (Figure II.6). Then, the OH groups can be divided in: (i) isolated free or single silanols, represented by  $\equiv\text{SiOH}$ ; (ii) geminal free or geminal silanols or silanediols, represented by  $=\text{Si}(\text{OH})_2$ ; and (iii) vicinal, or bridged, or OH groups bound through the hydrogen bond or H-bonded single silanols, H-bonded geminals, and their H-bonded combinations. On the  $\text{SiO}_2$  surface, there also exist surface siloxane groups or  $\equiv\text{Si-O-Si}\equiv$  bridges exposing oxygen atoms on the surface.



**Figure II.6:** Structural schemes of various OH sites found at the hydrated amorphous silica surface.

In the  $\text{SiO}_2$  the pore size distribution is very narrow being between 1 to 20 nm.<sup>16</sup> The classification of these pores is micro- and mesopores<sup>17</sup> and they are responsible for the high specific surface which ranges from 250 to 1000  $\text{m}^2/\text{g}$ .

The properties of silica can be altered by thermal or subsequent chemical treatment. We can find, in the surface of pure  $\text{SiO}_2$  even a maximum concentration of 8 Brönsted acid OH groups per  $\text{nm}^2$ .<sup>18</sup> They hydroxylated surface is hydrophilic and easily adsorbs moisture from the air. At temperature of 100 - 200°C this physically adsorbed water can be desorbed. This heating cause a partial dehydroxylation of the silica gel, reducing the number of OH groups per  $\text{nm}^2$  to approximately 5.5 (approximately 5 wt % silanol groups attached to 300  $\text{m}^2/\text{g}$  silica). Rising more the temperature the number of hydroxyl groups decreases continuously, until a 600-800°C and almost completely dehydroxylated silica with approximately 1 OH group per  $\text{nm}^2$  is left. From this silanol concentration onward the surface is hydrophobic.<sup>19</sup> This sequential alteration of properties of silica by thermal treatment can be seeing in the Figure II.7.



**Figure II.7:** Schematic representation of the dehydration of a silica gel surface.<sup>19</sup>

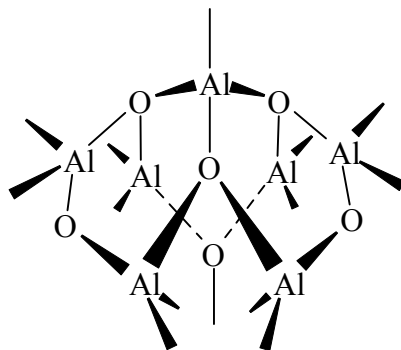
### II.3.1.2 *Silica modified with MAO*

Many approaches for supporting homogeneous catalysts have been reported in the literature<sup>13,20</sup> and the methods based on the silica chemical treatment with MAO or trimethylaluminium (TMA) prior to catalyst immobilization are believed to generate more active supported catalysts (in comparison with direct grafting). In such systems, it has been proposed that complexes be bonded to the support by loosely ionic interaction.<sup>21</sup>

In the polymerization reaction, the role of MAO is not completely elucidated. We know that MAO alkylates the precursor catalyst, generating coordinatively unsaturated cationic species. That process is made through the substitution of one halogen atom by an alkyl group and extraction of the second halogen atom. There are evidences that this type of compounds comprise the catalytic active species for olefin polymerization. MAO works as a counterion, keeping the catalytic species in a cationic state and playing the role of a non-coordinating anion. Trialkylaluminum ( $\text{AlR}_3$ ) may work in the same way, but the resulting anion too strongly coordinates to the catalyst cation, making the active site not available for the olefin insertion. Other functions have been attributed to MAO including the stabilization of the active species (counterion), prevention of bimolecular deactivation and water and oxygen milieu scavenger.<sup>22</sup>

Barron<sup>23</sup> characterized some alkylaluminumoxane  $[(\text{R}_2\text{Al})_2\text{O}]_n$  and  $(\text{RAlO})_n$ , containing *t*-Bu groups through some structural studies in the crystalline state, but the structure of aluminumoxanes with other alkyl groups, especially with methyl and ethyl ones, are still to be solved.<sup>24</sup> It is believed that the MAO possesses two or three acidic centers which are responsible for the reactions leading to oligomer formation, reaction with electron donors. Moreover, the direct elucidation of the structure and of the function of MAO is hindered by the presence of multiple equilibria such as disproportionation reactions between oligomeric chains as we can see in the Figure II.8. For the sake of simplicity MAO has been usually

represented as having linear chain or cyclic ring structures  $[\text{Al}(\text{Me})\text{-O}]_n$  containing three-coordinate aluminum centers.



**Figure II.8.** Structure of the MAO.

Commercially, the MAO is produced by the partial hydrolysis of TMA, also forming oligomeric molecules of MAO, and usually a significant amount of TMA associated with MAO.<sup>25</sup> This is evidenced by the equilibrium between both species, proposed by Eilertsen et al.<sup>26</sup> on FT-IR spectroscopy. Monitoring by DRIFTS and mass-spectrometric methods has evidenced that solid MAO releases TMA under heating between 20 and 250°C.<sup>27</sup>

Dos Santos et co-workers<sup>28</sup> studied silicas modified with MAO corresponding to 0.5–20.0 wt.% Al/SiO<sub>2</sub> and compare with commercial MAO-modified silica. Through that work, it was possible to conclude that the amount of Al supported in the surface of silica increases to a maximum of 10.0 wt.%. For values higher than the saturation level (higher than 10.0 wt.% Al/SiO<sub>2</sub>), the density of Al remains about 10–13 Al.nm<sup>-2</sup> values. It is worth mentioning that silicas treated at 450°C under vacuum present OH density close to 1.5 OH.nm<sup>-2</sup>.<sup>29</sup> In such case, for loadings below the surface saturation, there are roughly 1 or 2 Al atoms for each isolated silanol group. Nevertheless, such ratio is much higher for higher Al loadings, indicating that most of the Al atoms are not directly bound to silica surface.



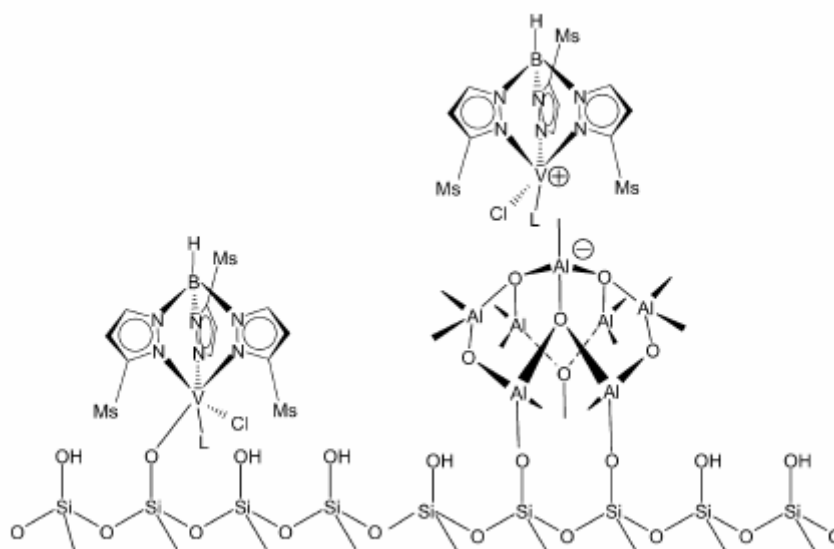
Submitting the supports to *in situ* thermal treatment for 1 h at 80 and 130°C, was evaluated the thermal stability of MAO-modified silicas. That temperature was chosen due to being employed for metallocene immobilization uses to polymerize in industrial plants.<sup>30</sup> Analyzing by IR, values smaller than the saturation level (10.0 wt.% Al/SiO<sub>2</sub>) its possible observe a reduction in the intensity of the bands corresponding to isolated OH and methyl groups. It seems that the presence of isolated silanol groups can promote the decomposition of surface methyl groups, probably by evolving of methane. No significative modification was perceived in the case of 10.0 wt.% Al/SiO<sub>2</sub>, probably due to the absence of free silanol groups, but the intensities of the bands of the silanol groups present an reduction. It is worth mentioning that during catalyst immobilization, part of such residual silanol groups might be consumed, reducing therefore such thermal instability in the case of MAO content lower than 10.0 wt.% Al/SiO<sub>2</sub>.

The Lewis acid sites on TMA- and MAO-modified silica were measured by CO adsorption at 77 K using transmission infrared spectroscopy.<sup>31</sup> The use of CO as probe molecule in our samples using DRIFTS measurements did not provide evidences of chemical interaction at 298 K. The CO generated species observed between 2300 and 2100 cm<sup>-1</sup> were promptly removed by vacuum.

Comparing the silica and the MAO-modified silica (small than 10.0 wt.% Al/SiO<sub>2</sub>), it is possible to conclude that the morphology of the supports is roughly kept identical. Nevertheless, for amount of Al at the saturation level it's observed the presence of abundant irregular fine particles. By EPMA analysis, it observed that the fine particles are constituted by practically pure aluminum. Similar results were reported for commercially high loaded silica (23 wt.% Al/SiO<sub>2</sub>).<sup>32</sup>

Casagrande et al. studied the immobilization and the *in situ* impregnation of the complexes tris(pyrazolyl)borate of vanadium<sup>33</sup> and titanium<sup>34</sup> on silica and MAO-modified

silicas. To the complex tris(pyrazolyl)borate imido vanadium the metal content in the supports, determined by XRF, remained between 0.045 and 0.098 mmol V/g support. An example for the immobilization of the catalyst in the MAO-modified silica is showed in the Figure II.9. These systems were shown to be active in ethylene polymerization using MAO or TiBa/MAO as activator (molar ratio of 1:1000). The catalyst activity was shown to depend of the support nature, being between 8.1 and 88.0 Kg of PE/mol[V].h.atm. To the *in situ* immobilization the catalyst activities increase, even in the presence of common alkylaluminum co-catalyst (TiBA). Resulting polyethylenes showed Mw higher than  $2.7 \times 10^6$  g/mol, suggesting the production of ultra-high molecular weight polymers. Other important question was bimodal distribution to GPC. Which indicates the presence of different actives sites, as showed in the Figure II.9.



**Figure II.9.** Representation of the immobilization of the complex tris(pyrazolyl)borate imido vanadium to the MAO-modified silica.

In the case of the Ti complex, the catalyst  $\{\text{Tp}^{\text{Ms}^*}\}\text{TiCl}_3$  ( $\text{Tp}^{\text{Ms}^*} = \text{HB}(3\text{-mesityl-pyrazolyl})_2(5\text{-mesityl-pyrazolyl})$ ) was active for ethylene polymerization when immobilized on silica and MAO-modified silicas. The amount of the catalysts in the supports, analyzed by XRF spectroscopy, varied between 0.10 and 0.18 mmol Ti/g support, these variations suggested that the complex preferably binds to the MAO present on the surface. The systems showed active to the ethylene polymerization reactions using a combination of TiBA and MAO as cocatalyst (1:1). The activities varied between 24.4 and 113.5 kg of PE/mol[Ti].h.atm and the supported catalyst generated *in situ* (under ethylene atmosphere) is roughly four times more active than supported. The viscosity-average molecular weights ( $\overline{M}_v$ ) of the PE's produced with the supported catalysts varying from 1.44 to  $9.94 \times 10^5$  g/mol with melting temperatures in the range of 125 – 140°C.

### **II.3.2 Nickel/ $\alpha$ -diimine complexes in heterogeneous processes**

There are several recent overviews of the area of olefin polymerization. Academic reviews of the  $\alpha$ -diimine chemistry<sup>10f,35</sup> complement other, more industrial perspectives.<sup>36</sup> The considerable additional activity in a number of industrial and academic laboratories has generated a body of literature of sufficient size that a review is now appropriate. It should be noted, however, that a very high percent of the information appears in the patent literature. With free, on-line patent databases, this material should now be readily available to most research labs in the world.

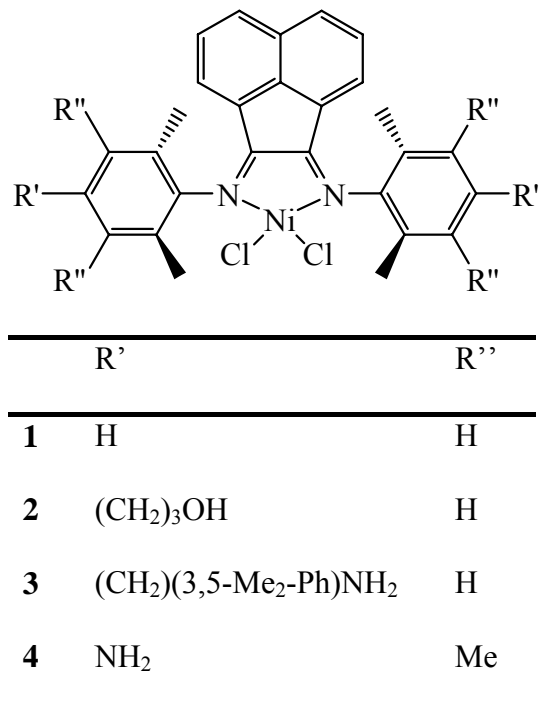
Recently, Ni(II) catalysts bearing  $\alpha$ -diimines ligands were supported on silica and utilized in the ethylene polymerization using toluene or hexane as solvent in the presence of MAO as cocatalyst. Those reactions using the catalyst pre-polymerized produced a polymer with density in the order of 0.40 g.cm<sup>-3</sup>.<sup>37</sup> Besides, researchers of the Exxon reported the use

of the supported catalyst  $\text{Ni}(\alpha\text{-diimine})\text{Cl}_2$  immobilized in MAO/silica and their application in polymerization of the ethylene in a reactor continuous of fluidized bed, producing polyethylene with  $T_m$  of  $91^\circ\text{C}$  and only 34 ramifications/1000 atoms of C, suggesting that these catalysts can be used to prepare particles regular morphologically without coalition risk or fouling.

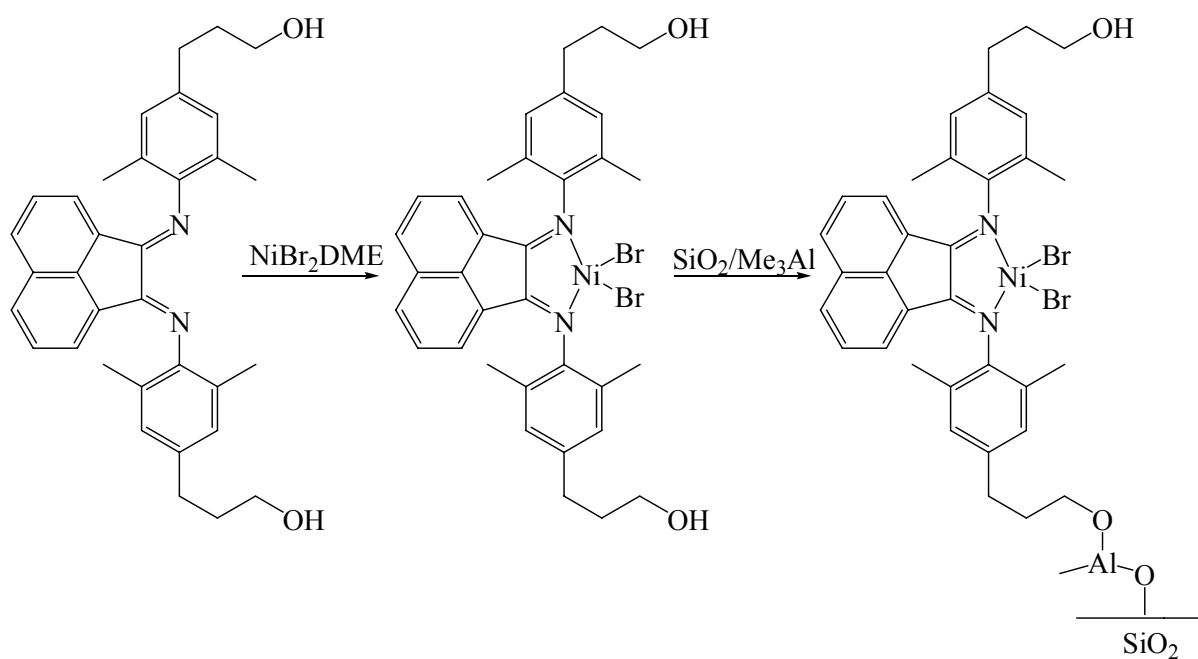
Brookhart et al. also investigated the catalytic activity of the Ni(II) precursors (**1** to **4**, Figure II.10) grafted on silica support pretreated with trimethylaluminium, and using chlorides ( $\text{Et}_3\text{Al}_2\text{Cl}_3$ ) as cocatalyst (Figure II.11). The supported catalysts were tested in slurry polymerization runs at 150 psig ethylene in pentane at temperatures between  $30$  and  $80^\circ\text{C}$  for 2 h (this time was chosen to simulate a common residence time in commercial polymerization processes). The resulting productivities of up to 820 kg of PE/mol[Ni].h.atm in 2 h at  $60^\circ\text{C}$  and 150 psig of ethylene, equivalent to an activity of around 2330 Kg of PE/mol[Ni].h.atm.<sup>38</sup> The polymers obtained showed molecular weights in the range of  $10^5$  and polydispersities around 3.5. The melting points of the polymer drop with increasing polymerization temperature. The same behavior had been observed with the unsupported catalysts.<sup>11,39</sup>

The complexes **5** to **8** (Figure II.12) were prepared by Chadwick et al. and tested in the polymerization of ethylene with  $\text{MgCl}_2/0.24.\text{AlEt}_{2,3}(\text{OEt})_{0,7}$  as support. These supported catalysts showed catalytic activities between 1190 and 7158 kg of PE/mol[Ni].h.atm (450 mL of light petroleum, 1 mmol of TiBA, at  $50^\circ\text{C}$  and an ethylene pressure of 5 bar for 1 h).<sup>40</sup> The polyethylenes obtained showed melting temperature between  $114$  and  $127^\circ\text{C}$  and 7 to 26 branches/1000 atoms of C where the proportion of methyl branches amounting to 82-87% of the total branching, is higher than has been reported for homogeneous systems.<sup>41</sup> The polymers obtained were free-flowing powders and there was no evidence of reactor fouling, and by scanning electron micrographs of the polymer particle morphology, demonstrating

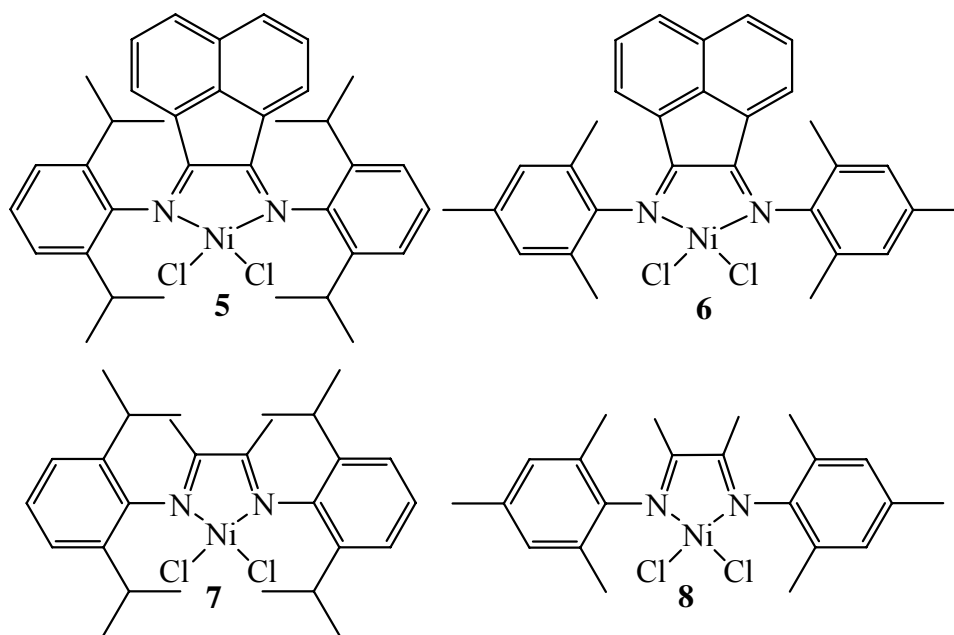
retention and replication of the spherical morphology of the original support during catalyst immobilization and polymerization.



**Figure II.10:** Structures of the complexes Ni( $\alpha$ -diimine) of Brookhart.



**Figure II.11.** Synthesis of Supported Complex **2**.



**Figure II.12:** Structure of the complexes of Brookhart.

## II.4 POLYMER BLENDS

### II.4.1 *General Aspects*

A large range of polyolefins with innovative chemical and physical characteristics have been produced by several classes of olefin catalyst precursors<sup>42,10e,10f,43</sup> since the discovery by Ziegler-Natta just over 40 years ago.<sup>3c,3e,44</sup> However, the industrial development of new polymers is expected to be rather limited in the future, and blending existing polymers seems to be the most effective way to design new polymeric materials with the desired combination of properties. Usually, polymer blends can be obtained either by a mechanical mixture of two or more melted polymers or by dissolving and mixing polymers at the desired composition followed by solvent evaporation.

Applications of polymer blends and multiphase polymer materials continue to enjoy growth in terms of market share, consumption, and employment within the plastics industry. This growth challenges the flexibility of materials suppliers to meet customer needs with new materials and reduced product development cycles. The futility of trial and error approaches to address these challenges led industry to solicit measurement tools and methods of analysis which enhance their efforts to understand and control resin compatibility, phase morphology, and blend material properties.

Polymer blends are mixtures of at least two macromolecular species, polymers and/or copolymers. For practical reasons, the name blend is given to a system only when the minor component content exceeds 2 wt%. Depending on the sign of the free energy of mixing, blends are either miscible or immiscible. In a global sense, polymer/polymer miscibility does not exist observed miscibility is always limited to a "miscibility window," a range of independent variables, composition, molecular parameters (viz., molecular conformation and configuration, molecular weight, molecular weight distribution, etc.), temperature, pressure,

and others. More than 1600 of these "miscibility windows" have been identified for two, three or four component blends.

In general, high-density polyethylene (HDPE) is used for applications that require hard products, and linear low-density polyethylene (LLDPE) is usually blended to improve flexibility.<sup>45</sup> Furthermore, LLDPE has been blended in small amounts (5-10 wt %) to reduce extruder back-pressure and increase output.<sup>46</sup> More recently, the concept to blend different polymers (two or more) in order to obtain a new product, with unique properties has been received special attention from academic and industrial field. This is consequence mainly of a large variety of applications of these polymeric materials, the low costs and great easiness to obtain them.

#### **II.4.2 Preparation methods**

The polymeric blends can be obtained by different methods, which control the values of Mw and MwD as:

- (i) The first one involves the physical mixture of polymers of different Mw.<sup>47</sup> This widely used solution show problems like the energy consumption, operational costs, and miscibility limitations.
- (ii) The second method involves the use of a series of reactors (multi-stage reactors), each one run under different polymerization reaction conditions.<sup>48</sup> This method can be used at pilot plant level, but it was considered as expensive, cumbersome and time consuming for industrial use.
- (iii) The third method utilizes the variation of operation conditions, such as temperature, comonomer concentration, and hydrogen pressure (non-steady-state polymerization), in a single reactor during polymerization.<sup>49</sup> This process is effective for laboratory-scale reactors, but is unlikely to be applied to the production of commodity polyolefins.



(iv) Finally, the fourth method consists of combining two or more types of catalysts to produce polymers with different and controlled Mw and MwD in a single reactor, this process is denominated of blends "*in situ*".<sup>50</sup> The advantages of this latter method, which is capable of producing more easily polymers with good properties by using just a single polymerization process, have received considerable attention by industrial laboratories as can be seen by the number of patents issued in recent years.<sup>51</sup>

This last process presents advantages in relation to the conventional methods as, for example, generate blends with different chemical and mechanical properties through the variation of the conditions reactionals in the polymerization process (temperature, concentrations molars, pressure, co-catalyst, etc.) and to promote more effective mixtures of the components than they decrease the incompatibility between the phases and they release thermal and mechanical treatments, which can generate some degradation of the polymers. Recently, studies revealed that the combination of two types different from catalysts promotes the formation of polymer with compared different characteristics than those obtained of the use of the catalysts separately.<sup>50d,52</sup>

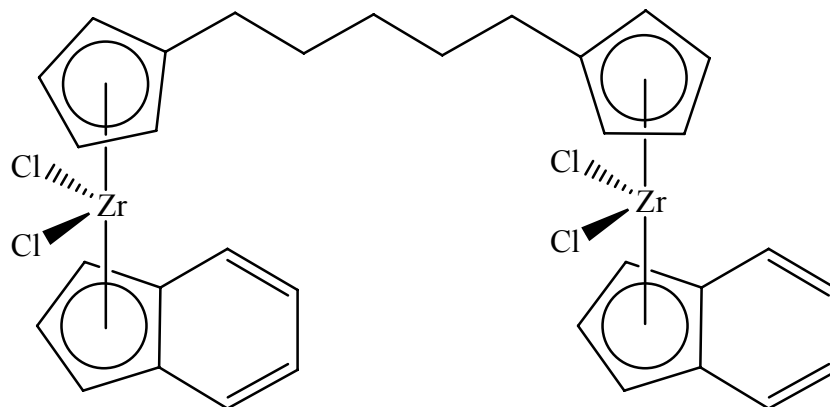
## II.5 THE *IN SITU* IMPREGNATION OF HETEROGENEOUS CATALYSTS

All well-know procedures for the impregnation of a complex to a support are time demanding, involving reaction and washing steps and final catalyst characterization. One problem present in this method is the effect of molecular deactivation that could happen when the catalytic precursor is supported and not used soon after, causing an decrease in the catalytic activity with time.

Soares and co-works<sup>53</sup> proposed an alternative methodology (called *in situ* impregnation) which uses a commercial immobilized cocatalyst. This approach consists in the direct addition of the catalyst solution to the MAO-supported silica inside the reactor, just before pressurizing with monomer. Normally, in these procedure it isn't required additional MAO as cocatalysts, because the activation of precursor are made *in situ*, by the Al present in the support. Therefore, this procedure avoids time consuming steps or addition of external MAO. Supported catalysts prepared by this *in situ* immobilization technique have been evaluated for ethylene homo- and copolymerization.

Soares and dos Santos<sup>54</sup> carried out the propylene polymerization with  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$  immobilized on commercial MAO-modified silica by the *in situ* supporting technique. A determination of adsorption isotherm for this system indicated that the saturation level is achieved at 2.0 wt.% Zr/SMAO. Catalyst systems were shown to be active in the absence of external MAO, being activated by common alkylaluminum cocatalysts as TEA, IPRA and TIBA. Best catalyst activity was observed in low concentration of IPRA (1.4 kg PP/g cat h). The resulting polymers showed MwD close to 2.1 and a variation of melting point between 135 and 140°C, showing higher molecular weights to the *in situ* supported systems than those synthesized with the homogeneous catalyst at the same Al/Zr ratio.

Park et al.<sup>55</sup> compared the *in situ* supported catalyst  $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$  (Figure II.13) with  $\text{Cp}_2\text{ZrCl}_2$  and  $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$  (also *in situ* supported) in a ethylene/1-hexene copolymerization.



**Figure II.13.** Structure of the catalyst  $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$

In homogeneous phase the catalyst  $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$  when used in the copolymerization, showed a negative comonomer effect, i.e. the activity decreased with comonomer incorporation, and it produced copolymer with a lower comonomer content than other catalysts, both of which were ascribed to the steric effect of the catalyst. In contrast to the homogeneous catalysts, when are used the *in situ* supported catalysts, the activity did not change much with the increase of 1-hexene content. The *in situ* supported catalysts produced copolymers with higher content of 1-hexene and lower melting point and crystallinity. The changes in the molecular weight and its distribution of the copolymer with *in situ* supporting became lower at low comonomer content but reached higher values at high concentrations than those from homogeneous catalyst.

Soares et al.<sup>56</sup> used the Brookhart catalyst Ni(diimine) (complex **5** of Figure II.12) supported *in situ* in MAO-modified silica and tested the catalytic activity and the polymer properties. The results demonstrate that the *in situ* supported catalyst is highly active, with

productivities reaching values close to 3000 Kg of PE/mol[Ni].h.atm. There is a maximum attainable activity when the temperature is raised. Thus, it implicitly considers the efficiency of catalyst activation on the support surface. The temperature dependence reported herein is similar to the observed for equivalent unsupported systems.<sup>12,57</sup> The authors could conclude that the *in situ* supported catalyst works as a heterogeneous system, producing polyethylene particles that replicate the support morphology very well. As seen by SEM images the geometry presented by the polymers was predominately spherical.

## II.6 OLEFIN OLIGOMERIZATION PROCESSES

### II.6.1 *General Aspects*

Linear alpha olefins (LAOs) are useful intermediates for amongst others the manufacture of co-polymers<sup>58,59</sup>, detergents, synthetic lubricants and plasticizer alcohols. Currently, LAO producers may broadly be grouped into two main categories, i.e. full range producers and on-purpose producers<sup>60</sup>, depending on the chemistry of the processes. More specifically, as the 1-C<sub>6-8</sub> can be used as additives for lubricants, the 1-C<sub>6-10</sub> provides odd-numbered linear primary alcohols and they can be converted to polyvinylchloride (PVC) plasticizers. The 1-C<sub>10-12</sub> can be epoxies to bifunctional derivatives or ethoxylates as nonionic surfactants. The 1-C<sub>14-16</sub> can be employed as surfactants as well as lubricant oil additives.

Industrially, the  $\alpha$ -olefins is obtained by thermal and catalytic cracking of paraffins (first for C<sub>2-5</sub> olefins and the second for higher C<sub>9-30</sub>  $\alpha$ -olefins manufactured in large scale), oligomerization of ethylene, dehydrogenation of paraffins, dimerization, metathesis of olefins and dehydrogenation of alcohols.<sup>61</sup> The three largest full range producers of LAOs via ethylene oligomerization are Shell, British Petroleum (BP) Amoco and Chevron Phillips.<sup>62</sup>

An inherent characteristic of the ethylene oligomerization processes catalyzed by transition metal is that they produce a mathematical distribution to the alpha olefins (Schulz - Flory or Poisson), these aspect does not match market demand. As are know, the alpha olefin market have different characteristics in terms of market size, growth, geography, fragmentation, technical services and logistics requirements and these product distribution provides a serious challenge to the producers. Nevertheless attempts have been made to change the mathematical distribution of olefins in favor of the higher value comonomer range (i.e. 1-C<sub>6</sub> and 1-C<sub>8</sub>),<sup>63</sup> but these modifications involve increased capital expenditure and

operational complexity. Actually, there are only a few on-purpose routes to LAOs due to the fundamentally different nature of the chemistry involved.<sup>60</sup>

- (i) In the Middle East is made the ethylene dimerisation to produce 1-butene.
- (ii) After 2003 Chevron Phillips (in the plant Q-Chem I of the project in Qatar) made the ethylene trimerization to produce comonomer grade 1-hexene.
- (iii) The Sasol facilities (in Secunda, South Africa) extract 1-hexene and 1-octene from Synthol streams. The effective difference between this process and the above-mentioned processes since it is not based on selective ethylene oligomerization, but though this can be regarded as an on-purpose route to specific LAOs.

### **II.6.2 *The discovery of the ethylene trimerization***

Manyik, Walker and Wilson, in Union Carbide Corporation (UCC), discover the process of the production of 1-hexene via ethylene trimerization, but the first to commercialize the technology was Chevron Phillips. Almost 40 years ago these researchers filed a patent<sup>64</sup> on continuous processes for the production of PE. They observed the trimerisation of ethylene to 1-hexene during the polymerization reaction using Cr(III) 2-ethylhexanoate (Cr(III) 2-EH) when activated by partially hydrolyzed tri-isobutylaluminium (PIBAO), which then co-polymerises with ethylene forming a polymer having butyl side chains. The publication of the results (using the same catalytic system) was made many years later by Manyik et al.<sup>65</sup>. In this work, it was possible to detect by a detailed chromatographic analysis of the solvent from these polymerization reactions revealed that 1-C<sub>4</sub>, 1-C<sub>6</sub>, 1-C<sub>8</sub> and 1-C<sub>10</sub> were produced with 1-C<sub>6</sub> being predominant. The ratio 1-C<sub>6</sub>:1-C<sub>4</sub> was about 25:1, but the 1-C<sub>6</sub> content was, however, only about 1.1% of the liquid sample. The analysis shows a production of additional 1-C<sub>10</sub> and a greatest number of branched decene isomers.

The rate of polymerization and 1-hexene formation suffers marked differences in relation of the dependence in pressure and temperature, being more sensitive to ethylene pressure than the rate of polymerization. Furthermore, the rate of 1-hexene formation seemed to be dependent on the square of the ethylene pressure, implying a second order reaction in ethylene. The authors concluded based on these results, that the production of 1-hexene would be via a metallocycle mechanism, to explain this second order dependence, not by a linear chain growth mechanism. The formation of the branched decene isomers can be also explained by this metallocycle mechanism, by the co-trimerization of two ethylenes and a 1-hexene molecule.

A large number of additives were also evaluated as possible poisons or promoters of the catalyst system. Isoprene, piperidine and chloroprene as well as conjugated dienes such as 2-methoxybutadiene, cyclohexadiene and 3-ethylidenecyclohexene poisoned the reaction. Addition of 1,2-dimethoxyethane (DME), however, led to a marked increase in 1-hexene formation.

### **II.6.3 *Homogeneous trimerization catalysts based on chromium***

The development of homogeneous trimerization catalysts based on chromium is summarized by the two major classes of ligands anionic and neutral multidentate ligands.

#### **II.6.3.1 *Cyclopentadienyl ligands***

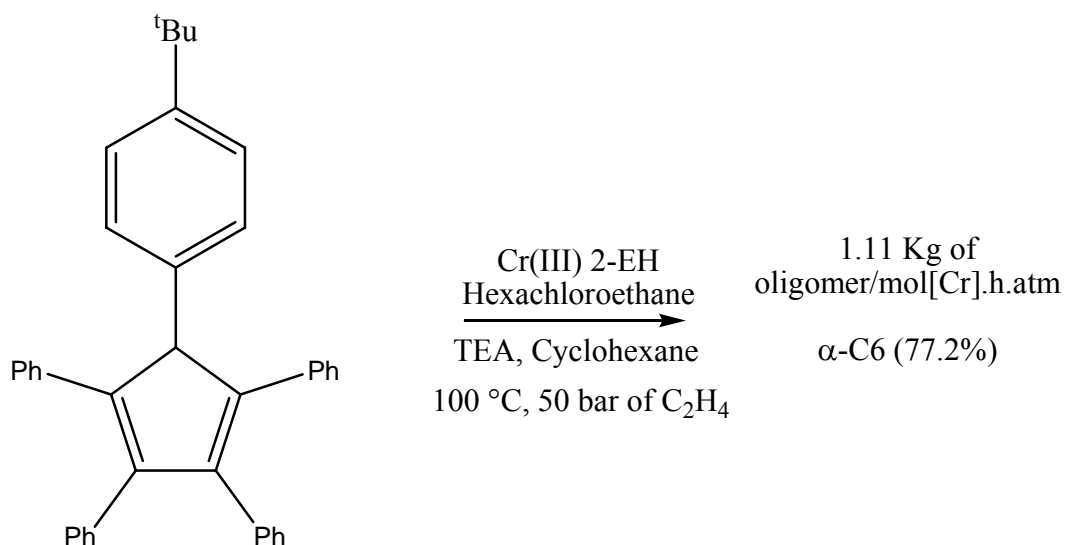
If we analyze in relation to the effects electronic and steric, the Cp ligands and pyrrolyl ligands are very similar.<sup>66</sup> By analogy, they should also be good ligands for chromium catalysed olefin trimerization. However, up until recently, chromium based

cyclopentadienyl complexes have only been shown to be active polymerization catalysts.<sup>10f,67</sup> Jolly et al.<sup>68</sup> used complexes of chromium metallocycle model with the ligand Cp to propose the potential existence of the metallocyclopentane and -cycloheptane intermediates for the trimerization mechanism. On the other hand, these Cp chromium metallocycle complexes were found to be very active ethylene polymerization catalysts, giving activities of 5.92 Kg of oligomer/mol[Cr].h.atm.

The Sasol Technology, to the contrary, showed that the introduction of bulky aromatic substituents onto the Cp ring can generate a highly active trimerization catalyst.<sup>69</sup> In terms of overall 1-C<sub>6</sub> selectivity, the best results were achieved using a catalyst prepared with Cr(III) 2-EH:ligand:hexachloroethane: TEA (molar ratios of 1:3:2.5:45) using 5-(4-*t*-butylphenyl)-1,2,3,4-tetraphenylcyclopentadienyl as ligand. The reaction conditions were temperature of 100°C and an ethylene pressure of 50 bars (Figure II.14). The catalyst activity was 1.11 Kg of oligomer/mol[Cr].h.atm. This gave a reaction mixture containing 99.5% liquid products comprising 0.5% C<sub>4</sub>, 93.5% C<sub>6</sub> (83% 1-C<sub>6</sub>, 77.2% 1-C<sub>6</sub> overall), and 6% C<sub>10+</sub>.

During these catalytic runs it was also formed a considerable quantity of internal hexenes, indicate that the selectivity to  $\alpha$ -hexenes was highly dependent on the substituents of the Cp ring. For example, the use of 5-(4'-*t*-butylphenyl)-1,2,3,4-tetraphenylcyclopentadienyl as ligand yielded to 83% 1-hexene whereas using 1,2,3,4-tetraphenylcyclopentadienyl yielded only 61.7% 1-hexene. Another parameter that influence the selectivity/activity is the reaction temperature, the lower of the temperatures promote a higher activity and 1-hexene selectivity in the C<sub>6</sub> fraction, but also promoting more PE and lower C<sub>6</sub> selectivity. For example, carried out a reaction of the Figure II.14, but at 70 °C, produced an overall 1-C<sub>6</sub> selectivity of 73.4% with a catalyst activity of 1.80 Kg of oligomer/mol[Cr].h.atm.





**Figure II.14.** Trimerization of ethylene made with Cr(III) 2-EH and the ligand 5-(4-*t*-butylphenyl)-1,2,3,4-tetraphenylcyclopentadienyl activated by TEA.

Due the high cost of substituted Cp ligands and the low 1-C<sub>6</sub> selectivity within C<sub>6</sub> fraction (17% internal hexenes) the system can be considered unviable to an economic viewpoint and the difficult separation of 1-C<sub>6</sub> from other C<sub>6</sub> isomers would influence negatively the process economic.

### II.6.3.2 *Chromium systems based on multidentate heteroatomic ligands*

The general characteristic of multidentate heteroatomic ligands is that they contain donor sites which form coordinate bonds with chromium. The tridentate systems can be subdivided into two systems were the pro-catalyst has a meridional or facial arrangement of the ligand. The first system yielding donors allowing for facile association– dissociation equilibrium and in general these systems provide very selective ethylene trimerization catalysts. An additional characteristic of these multidentate systems is that many are activated

by alkyl aluminoxanes, which due to their high cost, necessitate catalyst systems which are extremely active and selective for an economically practicable technology.

### II.6.3.3 *Ligands based on oxygen donors*

The first really selective ethylene trimerization system was patented more than a decade after Manyik's discovery that ethylene could be trimerized to 1-hexene. Briggs<sup>70</sup> (Long Range Catalyst Group of UCC) patented an ethylene trimerization catalyst system containing a chromium compound, a hydrolyzed hydrocarbylaluminium compound and a donor ligand (selected from hydrocarbyl isonitriles such as *t*-butyl isonitrile, amines such as tetramethylethylene diamine and ethers of the general type  $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ ), picking up the indication of Manyik et al. for donor ligands, such as dimethoxyethane (DME), to promote the reaction. Though, the best ethylene trimerization activities and selectivities were obtained still using DME as donor ligand. Briggs<sup>71</sup> later published the development of this catalyst, and in the best example, it used Cr(III) 2-EH, PIBAO and DME (molar ratio of 1:2:10) at 95 °C and 28 to 35 bars of ethylene in heptane as solvent to gave 74% generally 1-hexene selectivity and a catalyst activity  $4.0 \times 10^{-2}$  Kg of oligomer/mol[Cr].h.atm (TOF of  $1.2 \text{ Cr}^{-1} \cdot \text{s}^{-1}$ ). The residue of the product was PE with small quantities of C<sub>4</sub> and C<sub>8</sub>, the analysis of PE revealed no 1-hexene incorporation.

Levine and Karol<sup>72</sup> (UCC), studding the same system, showed that the presence of CO<sub>2</sub> could increase the efficiency of the trimerization catalyst toward 1-C<sub>6</sub> formation. The Idemitsu Chemical Company filed two patents in the mid 1990s related from UCC's discoveries about DME as donor ligand, but the difference between the systems is the activators used are an aluminum alkoxides. For example,<sup>73</sup> a solution of Cr(III) 2-EH and aluminum *t*-butoxide in cyclohexane was reacted with ethylene at 100 °C and 34 bar to give

the product containing 84% 1-C<sub>6</sub>, 3% 1-C<sub>8</sub>, 2% C<sub>10+</sub> and 11% PE. The catalyst activity was 10.1x10<sup>-2</sup> Kg of oligomer/mol[Cr].h.atm.

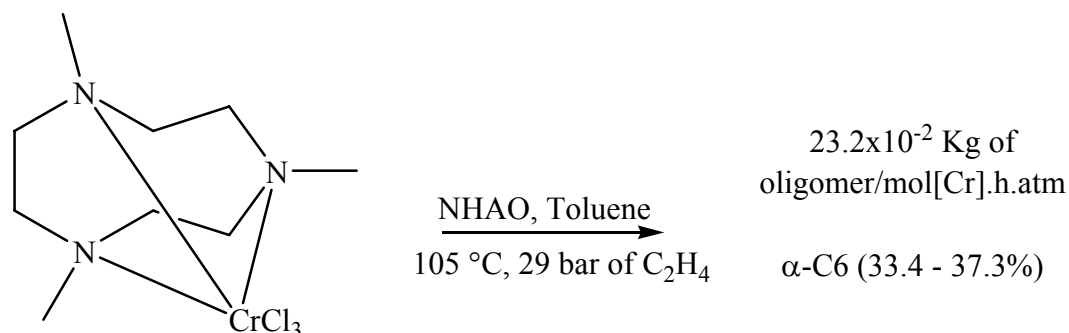
### **II.6.3.4      *Ligands based on nitrogen donors***

#### **II.6.3.4.1      *Triazacycloalkane ligands***

For the oligomerization of ethylene, the coordination facially to the chromium are sterically demanding when used the nitrogen-based ligands, such 1,4,7-trimethyl-1,4,7-triazacyclononane ligands. This was suggested by Wu<sup>74</sup>, reasoned that these ligands would permit both the trimerization and oligomerization of ethylene as, at the same time, inhibit polymerization. Wu describes, in a patent to Albemarle Corporation,<sup>74</sup> a process for the selective oligomerization of ethylene. The catalyst system contains complexes of Cr triazacyclononane using aluminoxanes as activators. The alpha olefins produced with this process afford a Schulz–Flory distribution, which is selectively augmented in 1-hexene, without the simultaneous formation of PE and excessive quantities of vinylidene olefins. The same reaction made in the absence of substitution on the nitrogens only gave PE, showing necessity of steric bulk for oligomerization over polymerization as well as the high reaction temperatures (ca. 30 °C) also favored oligomerization process.

As is observed for the Phillips catalyst system,<sup>75</sup> the catalyst lifetime was extended by the combination of catalyst components *in situ* in the reactor under ethylene pressure. As see in the Figure II.15, the catalyst [1,4,7-trimethyl-1,4,7- triazacyclononane]CrCl<sub>3</sub> and n-hexylaluminoxane (NHAO) (molar ratio of 1:80) was used to oligomerize ethylene at 105°C and 29 bar in toluene to give 9.4% C<sub>4</sub>, 39.3% C<sub>6</sub>, 10% C<sub>8</sub> and 41.3% C<sub>10+</sub> as a product. The selectivity for linear alpha olefins was 85 - 95% giving an activity of around 23.2x10<sup>-2</sup> Kg of

oligomer/mol[Cr].h.atm. The major product impurities were internal olefins, cyclic olefins and paraffins.

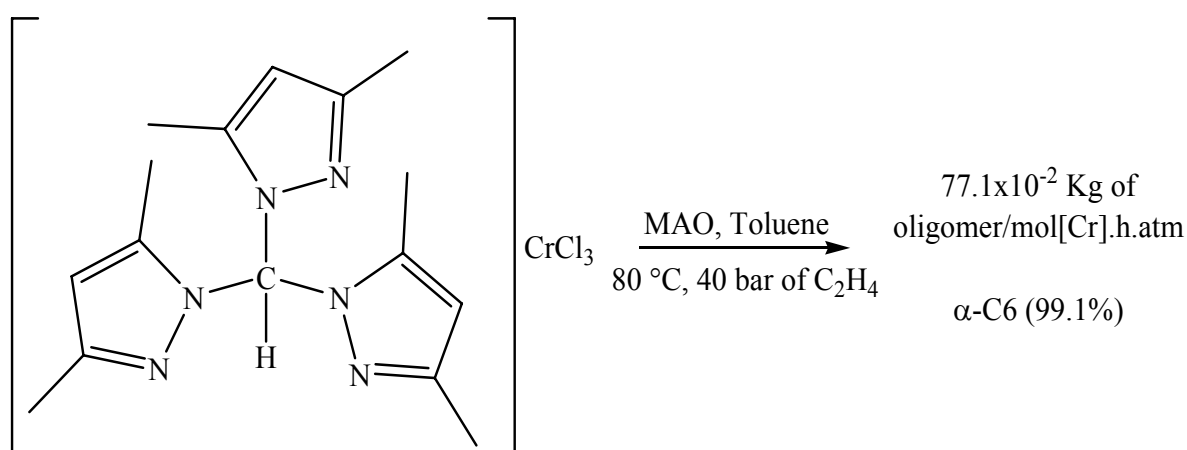


**Figure II.15.** Trimerization of ethylene made with [1,4,7-trimethyl-1,4,7-triazacyclononane]CrCl<sub>3</sub> activated by NHAO.

#### II.6.3.4.2 *Tris(pyrazolyl)methane ligands.*

Usually, the tris(pyrazolyl)methane ligands are used as complexes of copper(I), silver(I), cadmium(II), lead(II) and thallium(II),<sup>76</sup> however, Tosoh Corporation see that chromium complexes of these ligands, when activated by MAO or trialkyl aluminums, gave active and selective ethylene trimerization catalysts. To a patent<sup>77</sup> were synthesized four complexes (tris(3,5-dimethyl-1-pyrazolyl)methane chromium trichloride, tris(3-phenyl-5-methyl-1-pyrazolyl)methane chromium trichloride, tris(3-phenyl-1-pyrazolyl)methane chromium trichloride and tris(3-(4-tolyl)-1-pyrazolyl)methane chromium trichloride) and tested in ethylene trimerization upon activation with MAO or mixtures of MAO and *n*-octyl<sub>3</sub>Al or *i*-Bu<sub>3</sub>Al, gave active and selective catalysts. These complexes were prepared by reacting the respective tris(pyrazolyl)methane ligands with CrCl<sub>3</sub>(THF)<sub>3</sub> in THF as solvent and were found to coordinate facially to the chromium.

In relation at the catalytic activity, the best result was accomplished using tris(3,5-dimethyl-1-pyrazolyl)methane chromium trichloride complex activated by MAO (molar ratio of 1:360) at 80°C and 40 bar ethylene pressure (Figure II.16). This gives a reaction mixture of 0.1% C<sub>4</sub>, 99.6% C<sub>6</sub> (99.1% 1-C<sub>6</sub>) and 0.3% C<sub>8+</sub> and showed the catalytic activity of the 77.1x10<sup>-2</sup> Kg of oligomer/mol[Cr].h.atm.



**Figure II.16.** Trimerization of ethylene made with tris(3,5-dimethyl-1-pyrazolyl)methane chromium trichloride activated by MAO.

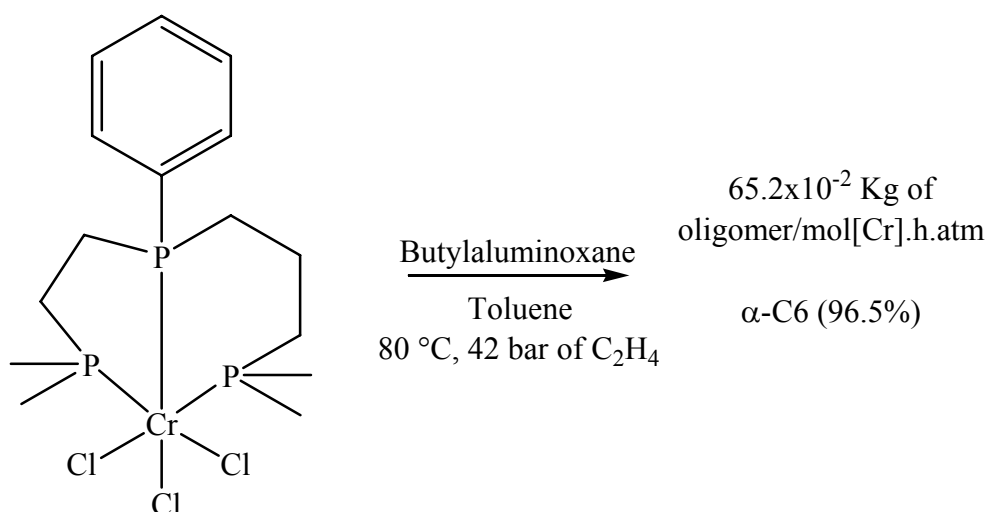
The tests systems provide relatively remarkable 1-hexene selectivities and good catalyst activities. In contrast to many other nitrogen-based ligand systems, tris(pyrazolyl)methane ligands are stable and easy to handle.

### II.6.3.5 *Ligands based on phosphorus donors, the polydentate phosphine ligands*

The ethylene trimerization catalyst involving chromium complexes of polydentate phosphines (represented by R<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>P(R'))(CH<sub>2</sub>)<sub>m</sub>PR<sub>2</sub>) and aluminoxane as co-catalyst was

developed by Amoco Corporation.<sup>78</sup> The x-ray structural analysis discovered an octahedral geometry of the complexes with meridional arrangement of the ligand.

The best catalytic results are showed in the Figure II.17, were obtained using as ligand (2-dimethylphosphinoethyl)(3-dimethylphosphinopropyl) phenylphosphine to forme the chromium complex that was activated by butylaluminumoxane (BuAO) (molar ration of 1:214) at 42 bar of ethylene and 80°C in toluene. This afforded a reaction mixture of 1% C<sub>4</sub>, 97.7% C<sub>6</sub> (96.5% 1-C<sub>6</sub>), 1% C<sub>10</sub> and 0.3% PE, showed the catalytic activity of 65.2x10<sup>-2</sup> Kg of oligomer/mol[Cr].h.atm.



**Figure II.17.** Trimerization of ethylene made with (2-dimethylphosphinoethyl)(3-dimethylphosphinopropyl) phenylphosphine chromium trichloride activated by BuAO.

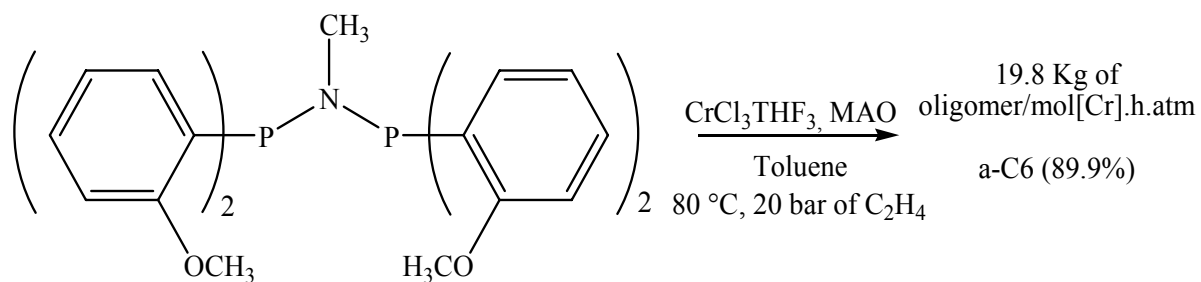
### II.6.3.6 *Ligands based on mixed P and N donors*

#### II.6.3.6.1 *Diphosphazane ligands – (R<sub>2</sub>PN(R)PR<sub>2</sub>)*

The ligands diphosphazane have earlier been related as complexes of Pd to give ethylene/CO copolymerization catalysts<sup>79</sup> and as complexes of Ni to give ethylene

polymerization catalysts.<sup>80</sup> Recently the British Petroleum has patented<sup>81</sup> and published<sup>82</sup> the first catalyst system of chromium-based with diphosphazane ligands ( $\text{Ar}_2\text{PN}(\text{Me})\text{PAr}_2$  where Ar is an *o*-methoxy-substituted aryl group) that when activated with MAO provide very active and selective ethylene trimerization catalysts.

Incredibly, the best catalytic activities for trimerization of ethylene were found with very low concentrations of Cr and ligand. For example, using 0.0025 mmol  $\text{CrCl}_3(\text{THF})_3$  and  $(2\text{-methoxyphenyl})_2\text{PN}(\text{Me})\text{P}(2\text{-methoxyphenyl})_2$  activated by MAO (molar ratio of 1:300) at 80°C and 20 bar in toluene (Figure II.18) the catalyst gave 90%  $\text{C}_6$  (89.9% 1- $\text{C}_6$ ), 1.8%  $\text{C}_8$  and 8.5%  $\text{C}_{10}$ , not accounting PE formation and the catalyst activity was, extraordinarily, 19.8 Kg of oligomer/mol[Cr].h.atm, some two orders of magnitude superior than various systems.

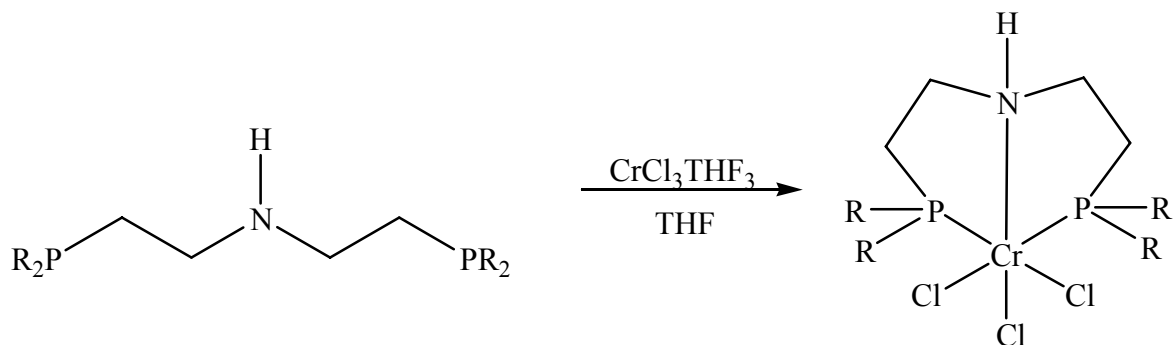


**Figure II.18.** Trimerization of ethylene made with  $\text{CrCl}_3(\text{THF})_3$  and  $(2\text{-methoxyphenyl})_2\text{PN}(\text{Me})\text{P}(2\text{-methoxyphenyl})_2$  activated by MAO.

#### II.6.3.6.2 Bis-phosphinoamine ligands – $(\text{R}_2\text{PCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{PR}_2)$ .

The Cr(III) complexes of tridentate ligands of the type bis-phosphinoamine  $(\text{R}_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{PR}_2)$  were recently patented<sup>83</sup> and published<sup>84</sup> by Sasol Technology on a trimerization of ethylene reaction. These complexes are synthesized by

reaction of the bisphosphino amine ligands with  $\text{CrCl}_3(\text{THF})_3$  at room temperature, as seemed in the Figure II.19.

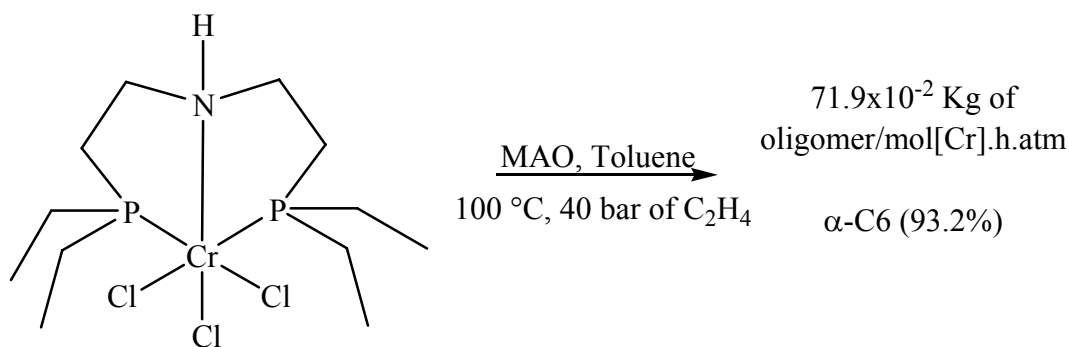


**Figure II.19.** Synthesis of Cr(III) complexes with the ligand bis-phosphinoamine ( $\text{R}_2\text{PCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{PR}_2$ ).

They are extremely active and selective for the production of 1- $\text{C}_6$  when activated with MAO. The initial efforts to augment the activity of the system are focus on the modification of the R groups on the phosphorous atoms. With a reduction of sterically bulky led to increased activity and excellent 1- $\text{C}_6$  selectivities and the augmentation of sterically bulky decreased activity and increased PE production.

In terms of the catalytic activity for trimerization of ethylene, the best was achieved using [bis-(2-diethylphosphino-ethyl)amine] $\text{CrCl}_3$  activated by MAO (molar ratio 1:850) at 100°C and 40 bar ethylene in toluene. This afforded a reaction mixture containing 94%  $\text{C}_6$  (93.2% 1- $\text{C}_6$ ) and 2.1% PE as see in the Figure II.20.



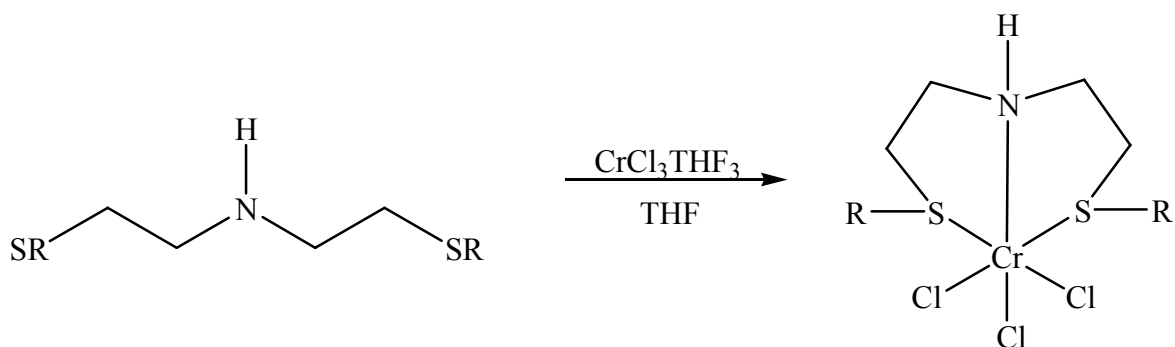


**Figure II.20.** Trimerization of ethylene made with [bis-(2-diethylphosphinoethyl)amine]CrCl<sub>3</sub> activated by MAO.

### II.6.3.7 Ligands based on mixed S and N donors, the bis-sulphanylamine ligand – (RSCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>-CH<sub>2</sub>SR).

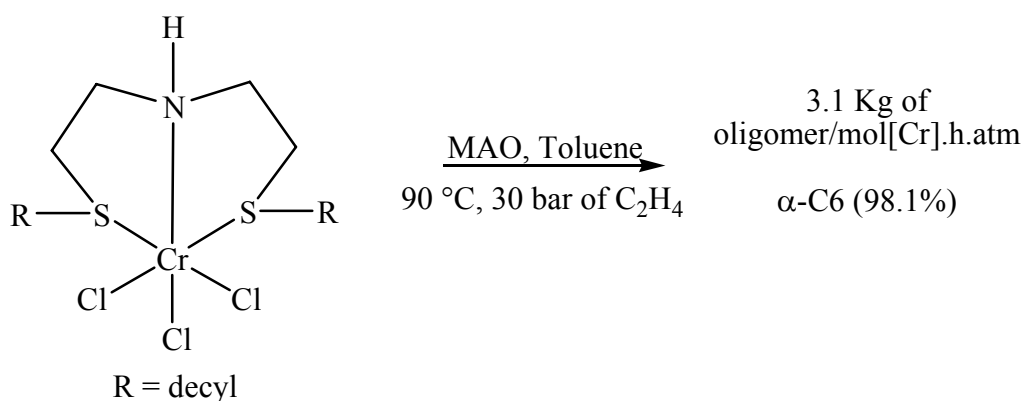
Bollmann et al.,<sup>85</sup> searching for options to P-based ligands, reasoned that, as the phosphine pendants of the bis-phosphinoamine system (Figure II.20) act as soft donor atoms capable of facile association–dissociation equilibria, the donor properties of thioether groups should be similar. Primarily, alkyl SNS ligands with low steric demand were searched due to being similar structurally and that the substituents on the PNP systems gave good results.

Inexpensive reagents are used to prepare the [bis-(2-alkylsulphanyl-ethyl)-amine]CrCl<sub>3</sub> complexes in good yields, the reaction of the SNS ligand with CrCl<sub>3</sub>(THF)<sub>3</sub> is made at room temperature to give the corresponding complex in high yields as seen in the Figure II.21.



**Figure II.21.** Synthesis of Cr(III) complexes with the SNS ligand bis-(2-alkylsulphanyl-ethyl)- amine.

The [bis-(2-decylsulphanyl-ethyl)-amine]CrCl<sub>3</sub> complex, activated with MAO (molar ratio of 1:280), were used to trimerization reaction of the ethylene at 90°C and 40 bar ethylene in toluene, giving 98.4% C<sub>6</sub> (98.1% 1-C<sub>6</sub>) as see in the Figure II.22. The quantity of PE produced was 0.16% and the catalyst activity was 3.1 Kg of oligomer/mol[Cr].h.atm.



**Figure II.22.** Trimerization of ethylene made with [bis-(2-decylsulphanyl-ethyl)-amine]CrCl<sub>3</sub> activated by MAO.

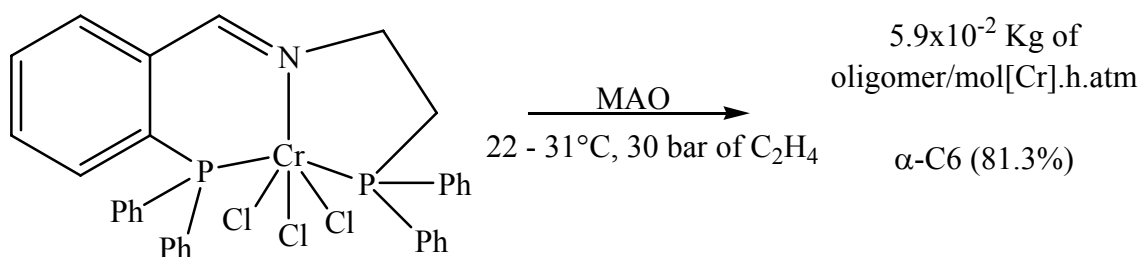
In relation of the sterics effects, if compare the groups R as ethyl or decyl, the results were superior to the complex with the decyl group at those obtained using the less soluble

[bis-(2-ethylsulphanyl-ethyl)-amine]CrCl<sub>3</sub> complex. Other point appreciably, was that more soluble complexes could be activated with very low quantities of MAO (molar ratio between 1:30 - 100). Due to the high cost of MAO, this has positive implications for the process economics.

### II.6.3.8 Ligands based on mixed PNP and PNS imines

Ethylene trimerization results, using Cr(III) complexes of mixed N, P, O and S containing imines and amines, have been reported by Bluhm et al.<sup>86</sup>. These catalysts when activated by MAO gave 1-hexene in reasonable selectivity (though at low activity), or produced mostly PE.

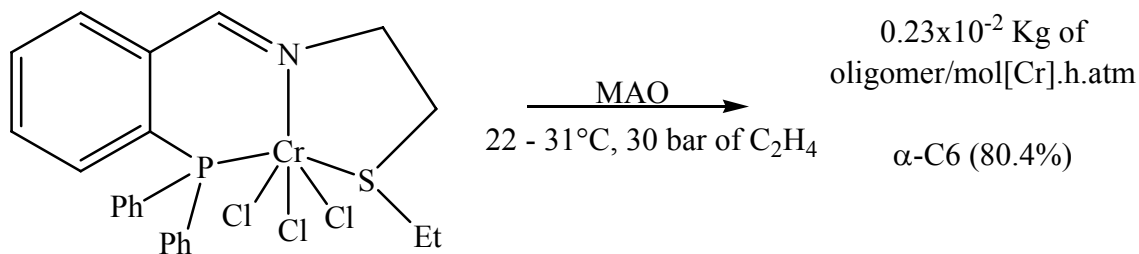
In the best trimerization catalyst, the PNP imine complex of Cr activated with MAO (molar ratio 1:100) at 22 - 31°C and 30 bar ethylene to afford 83% C<sub>6</sub> (81.3% 1-C<sub>6</sub>) and 17% PE as see in the Figure II.23. The catalyst activity was 5.9x10<sup>-2</sup> Kg of oligomer/mol[Cr].h.atm.



**Figure II.23.** Trimerization of ethylene made with PNP imine complex of Cr activated by MAO.

Other complex tested in ethylene trimerization was the PNS imine complex of Cr activated with MAO (molar ratio 1:100) at 22 - 31°C and 30 bar ethylene to give 82% C<sub>6</sub>

(80.4% 1-C<sub>6</sub>) and 18% PE as see in the Figure II.24. In this case, the catalyst activity was lower, incoming at 0.23x10<sup>-2</sup> Kg of oligomer/mol[Cr].h.atm.

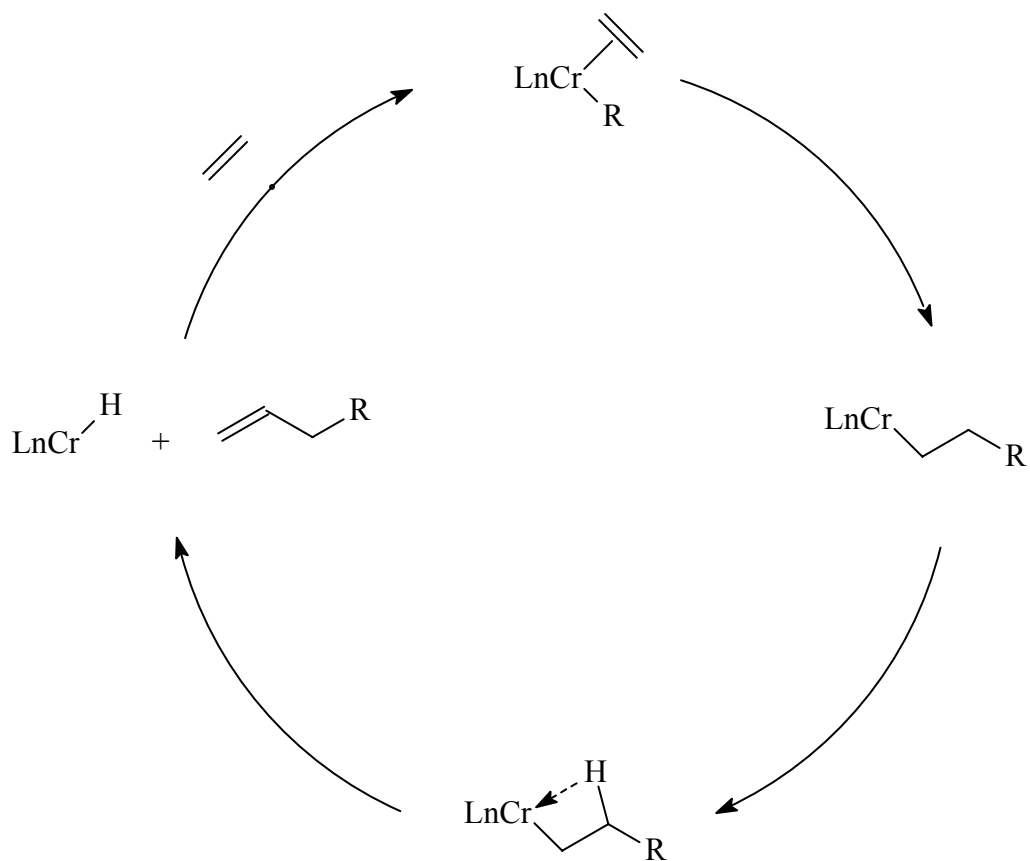


**Figure II.24.** Trimerization of ethylene made with PNS imine complex of Cr activated by MAO.

## II.6.4 Mechanistic considerations and molecular modelling

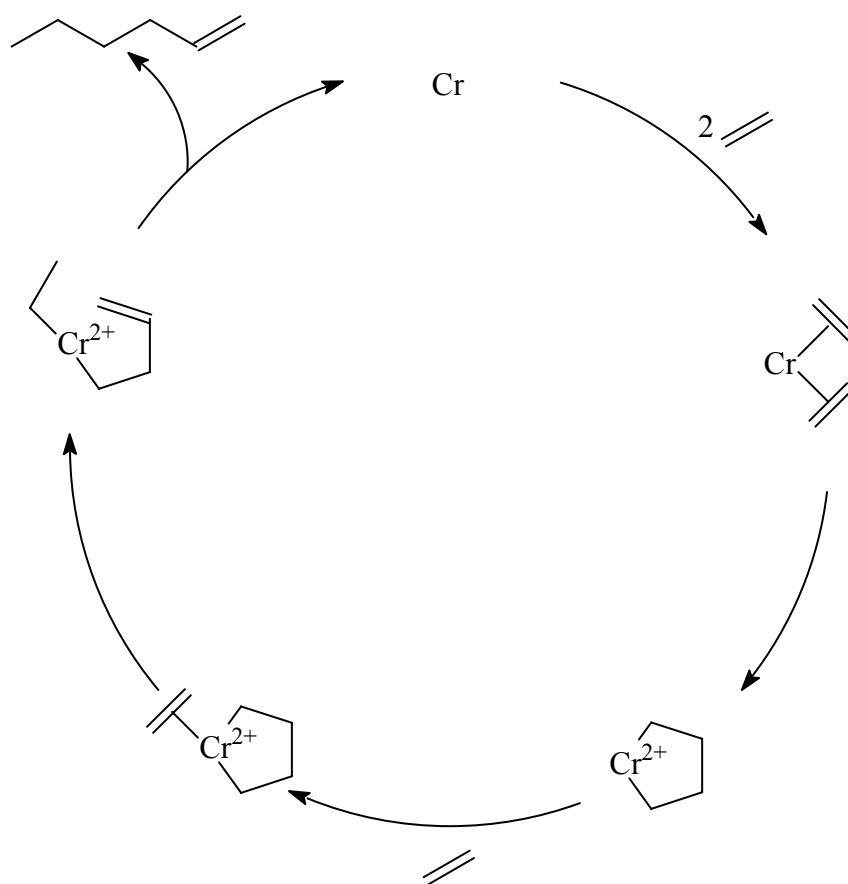
### II.6.4.1 Historical development of the metallocycle mechanism

The oligomerization of ethylene to linear alpha olefins was well understood before to the discovery of ethylene trimerization. Normally, the product distribution of the linear alpha olefin processes forms a statistical series of oligomers following a Schulz–Flory<sup>87</sup> or Poisson distribution. Cossee and Arlman,<sup>88</sup> proposed a mechanism that explained these distribution by chain growth via ethylene coordination pursued by insertion into a transition metal alkyl bond. The chain termination occurred via β-hydrogen transfer to the metal to form a metal hydride species, liberating the linear alpha olefin as see in the Figure II.25.



**Figure II.25.** Mechanism of formation of linear alpha olefins proposed by Cossee and Arlman.<sup>88</sup>

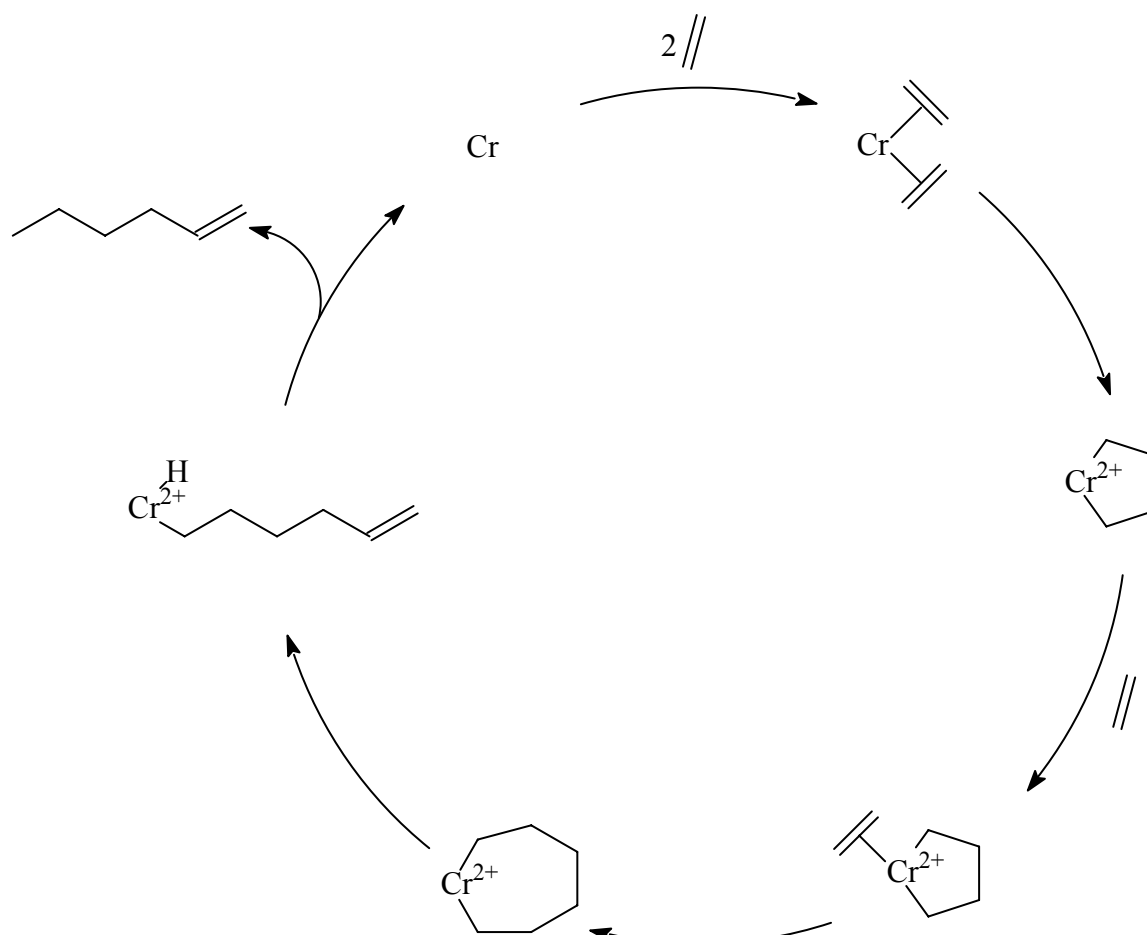
The existence of Pt(II) metallocycles was demonstrated by McDermott et al.<sup>89</sup> in the early 1970s, in that way showing in principle that metallocyclic reaction intermediates could exist. Based in these advance, Manyik et al.<sup>65</sup> proposed in 1977 the first metallocycle-based oligomerization mechanism for the selective chromium catalyzed trimerization of ethylene to 1-hexene as see in the Figure II.26.



**Figure II.26.** Mechanism of trimerization of ethylene metallocycle-based proposed by Manyik et al.<sup>65</sup>

The first step of the mechanism involved the coordination of two ethylene molecules, followed by the formation of the chromacyclopentane, been not identified a bigger metallocycle. The authors proposed a  $\beta$ -hydrogen transfer from the chromacyclopentane to a third coordinated ethylene to yield an intermediate called chromium butenyl ethyl. The liberation of 1-hexene occurs via a reductive elimination from this di-alkyl intermediate. Kinetic experiments conducted by these same authors indicated that the reaction was second order with respect to ethylene, and thus the formation of the chromacyclopentane was proposed as the rate-determining step.

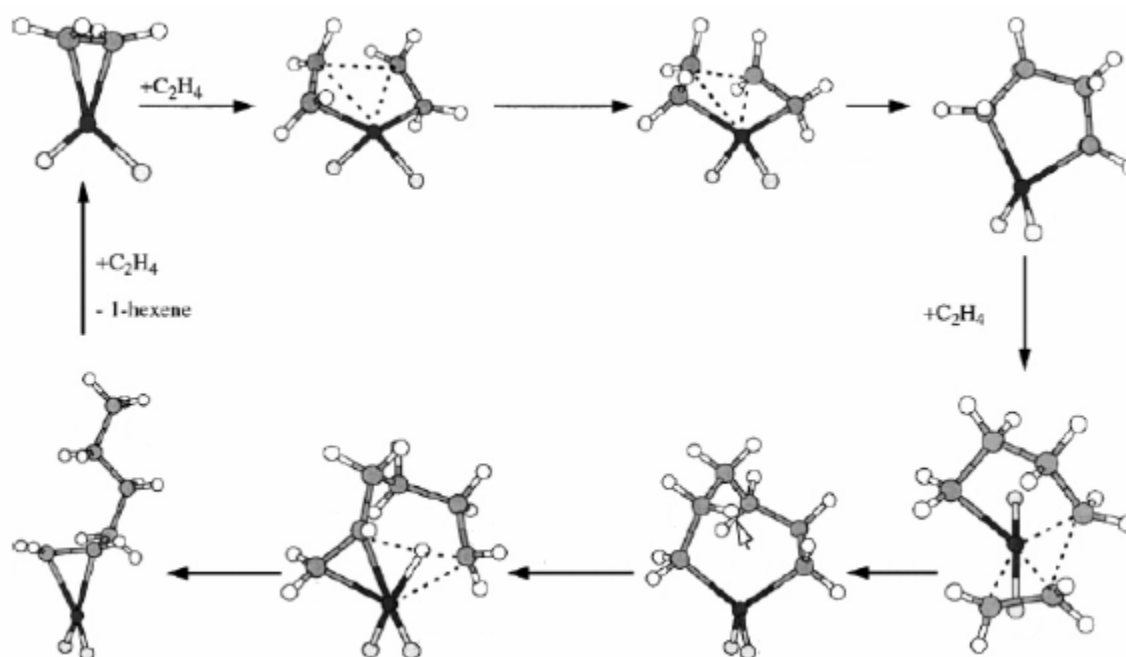
The mechanism involving the chromium metallocyclopentane species were also invoked in the activation of the commonly known Phillips  $\text{CrO}_3/\text{SiO}_2$  catalyst for ethylene polymerization.<sup>90</sup> Briggs<sup>71</sup> postulated the in place of a  $\beta$ -hydrogen transfer to ethylene, fast insertion of ethylene into the metallocyclopentane species occurs to form a metallocycloheptane. At this stage, ring opening occurs via the formation of a chromium hexenyl hydride species, which undergoes reductive elimination to liberate 1-hexene and the active catalytic species (Figure II.27).



**Figure II.27.** Mechanism of trimerization of ethylene for the Phillips  $\text{CrO}_3/\text{SiO}_2$  catalyst proposed by Briggs.<sup>90</sup>

The oxidation state of the chromium, during the various stages of the catalytic cycle, is an important aspect of the mechanism. Oxidative addition of the first two ethylene molecules to form a metallocyclopentane species involves an increase in the formal oxidation state from Cr to Cr<sup>2+</sup>. In contrast, 1-hexene liberation via reductive elimination involves a decrease from Cr<sup>2+</sup> to Cr. This is not yet well understood, but Cr(III)/Cr(V),<sup>91</sup> Cr(I)/Cr(III),<sup>65,92</sup> and Cr(II)/Cr(IV)<sup>93</sup> couples have been proposed to date.

Espelid and Børve<sup>94, 95</sup> performed the *abinitio* calculations to show the ethylene trimerization to 1-hexene in the Phillips CrO<sub>3</sub>/SiO<sub>2</sub> catalyst, when used the tetrahedral CrO<sub>3</sub>Si<sub>2</sub>H<sub>4</sub> mononuclear cluster. The mechanism is presented in the Figure II.28.



**Figure II.28.** Mechanism of trimerization of ethylene for the tetrahedral CrO<sub>3</sub>Si<sub>2</sub>H<sub>4</sub> mononuclear cluster, here only partially reproduced as a -O-Cr-O- fragment of the ring.<sup>95,96</sup>



### **III. EXPERIMENTAL**

---

### III.1 General Procedures

All manipulations were performed using standard vacuum line and Schlenk techniques under an argon atmosphere. Dimethylformamide (DMF), tetrahydrofuran (THF), toluene and hexane were distilled from sodium benzophenone ketyl. Diglyme (2-methoxyethylether) was distilled with potassium. All solvents were stored under argon or *in vacuum* before use. Ni(diimine- $\alpha$ )Cl<sub>2</sub> (diimine- $\alpha$  = 1,4-bis(2,6-diisopropylphenyl)acenaftenodiimine) (**1**)<sup>96</sup> and Tp<sup>Ms\*</sup>TiCl<sub>3</sub> (Tp<sup>Ms\*</sup> = tris[(3-mesitylpyrazolil)<sub>2</sub> (5-mesitylpyrazolil)]borate) (**2**)<sup>97</sup> were prepared according to procedures published in the literature. Silica (Grace 948, 255 m<sup>2</sup>.g<sup>-1</sup>) was activated under *vacuum* ( $P < 10^{-4}$  mbar) for 16 hours at 100°C. The support was then cooled to room temperature under dynamic *vacuum* and stored under dried argon. The commercial silica (Witco) modified with 23% of methylaluminoxane (MAO) was used as received. Ethylene (polymer grade, White Martins) and argon were deoxygenated and dried by passage through columns of BTS (BASF) and activated molecular sieves (3 Å) prior to use. MAO (Witco, 5.21 wt.% toluene solution) was used as received.

### III.2 Preparation of the supported Catalysts

#### III.2.1 Preparation of SiO<sub>2</sub>/MAO (4.0 and 8.0 wt.-% Al/SiO<sub>2</sub>)<sup>98</sup>

MAO-modified silica was prepared by impregnating 1.0 g of thermally treated silica Grace 948 with a solution of MAO in toluene corresponding to 4 and 8 wt.% Al/SiO<sub>2</sub> at room temperature for 3 h under stirring. The solvent was removed under vacuum and the solid was dried.

### III.2.2 General procedure for preparation of Ni(II) supported catalysts

In a typical support catalyst procedure, Ni(diimine- $\alpha$ )Cl<sub>2</sub> toluene solution corresponding to 0.5 wt.% V/support was cannula-transferred at room temperature onto inorganic support (1.0 g) toluene slurry. After 3h, the slurry was then filtered through a fritted disk. The resulting solids were washed several times (ca. 5 × 10 mL) with toluene at 50°C (until resulting in a colorless eluate), with hexane, and finally dried under vacuum for 24 h.

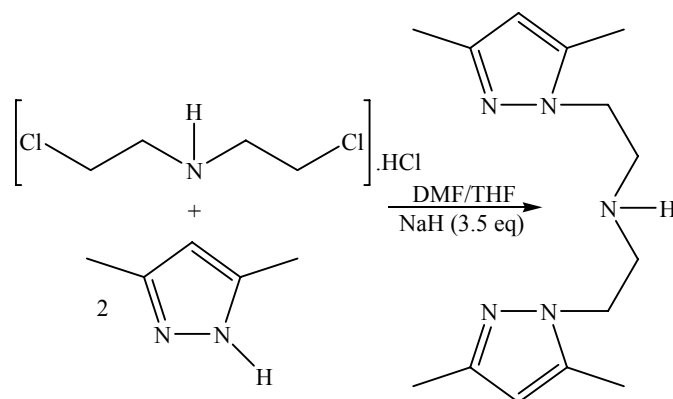
The amounts of Ni calculated by XRF for the heterogeneous systems were:

- Ni(diimine- $\alpha$ )Cl<sub>2</sub>/SiO<sub>2</sub> (**S1**): 128  $\mu$ mol of Ni/g of SiO<sub>2</sub>.
- Ni(diimine- $\alpha$ )Cl<sub>2</sub>/MAO/SiO<sub>2</sub> (4.0 wt.% Al/g support) (**S2**): 145  $\mu$ mol of Ni/g of SiO<sub>2</sub>.
- Ni(diimine- $\alpha$ )Cl<sub>2</sub>/MAO/SiO<sub>2</sub> (8.0 wt.% Al/g support) (**S3**): 165  $\mu$ mol of Ni/g of SiO<sub>2</sub>.
- Ni(diimine- $\alpha$ )Cl<sub>2</sub>/MAO/SiO<sub>2</sub> (23.0 wt.% Al/g support) (**S4**): 71  $\mu$ mol of Ni/g of SiO<sub>2</sub>.

### III.3 Synthesis of Chromium compounds

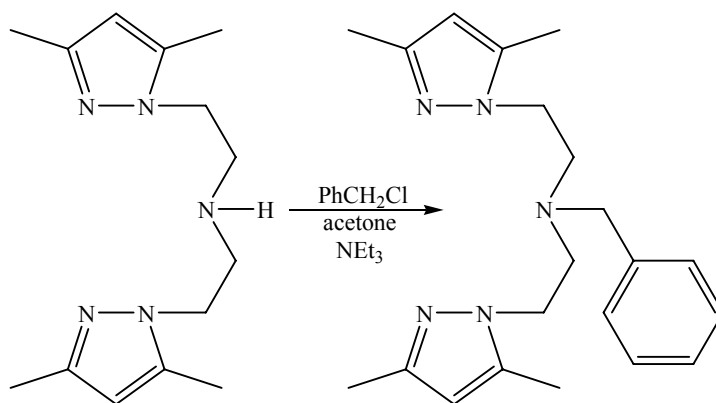
#### III.3.1 Syntheses of Ligands

**Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine.**<sup>99,100</sup>



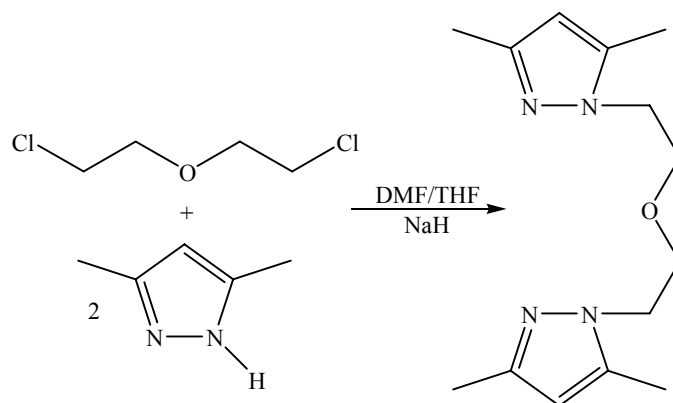
Under an argon atmosphere, 3,5-dimethylpyrazole (3.66 g, 0.038 mol) was slowly added to a suspension of NaH (1.61 g, 0.066 mol) in a mixture of DMF (35 mL) and THF (25 mL). The reaction mixture was stirred at 70 °C for 2 h. To the resulting solution was added a solution of bis(2-chloroethyl)amine hydrochloride (3.40 g, 0.019 mol, previously dried *in vacuum* at 40°C for 5 h to remove traces of water) in DMF (10 mL). Strong evolution of H<sub>2</sub> was immediately observed, followed after some minutes by the precipitation of NaCl. The reaction mixture was stirred for 30 h at 70°C, yielding a cream white suspension that was cooled and filtered. The filtrate was evaporated to dryness *in vacuum*, the wine-red oily residue resulting was dissolved in CHCl<sub>3</sub> (25 mL), washed with saturated aqueous NaCl (3 x 25 mL) and with water (3 x 25 mL). The solution was dried over MgSO<sub>4</sub>, concentrated *in vacuum* and the oil was solubilized in methanol and added to hot water (80 °C). Crystallization occurred upon slow cooling to give white needles of Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (2.63 g, 53%). <sup>1</sup>H NMR(CDCl<sub>3</sub>, 298 K): δ 2.17 (6 H, s), 2.19 (6 H, s), 2.95 (4 H, t, J = 6.09 Hz), 4.00 (4 H, t, J = 6.11 Hz), 5.74 (2 H, s). <sup>13</sup>C NMR: δ 10.92, 13.37, 48.29, 49.17, 104.75, 138.96, 147.34.

**Benzylbis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine.**<sup>100</sup>



To a solution containing bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (0.34 g, 1.30 mmol) in acetone (3.5 mL) was added benzyl chloride (0.16 g, 1.30 mmol) and triethylamine (0.12 g, 1.20 mmol). The reaction mixture was refluxed for 3 h. The solvent was evaporated *in vacuo*, and the resulting oil was dissolved in dichloromethane (9 mL), washed 2 times with brine (7 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration, dichloromethane was evaporated and the resulting oil was purified by column chromatography. The solvent was then removed on a rotary evaporator to give a benzylbis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine as brown oil (0.33 g, 72%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K): δ 2.14 (6H, s), 2.21 (6H, s), 2.91 (4H, t, J = 7.16 Hz), 3.66 (2H, s), 3.93 (4H, t, J = 6.84 Hz), 5.76 (2H, s), 7.25 (5H, s).

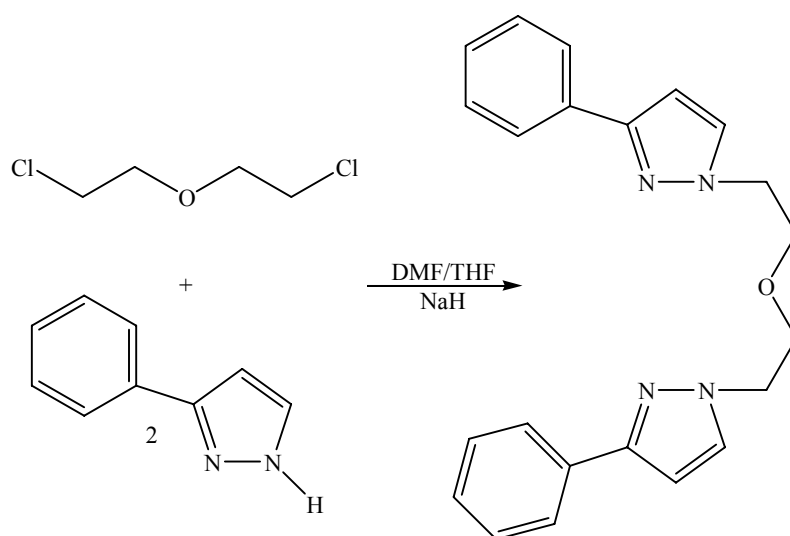
**Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether.<sup>99</sup>**



Under an argon atmosphere, 3,5-dimethylpyrazole (3.20 g, 0.033 mol) was slowly added to a suspension of NaH (1.21 g, 0.050 mol) in dry DMF (35 mL) and dry THF (25 mL). The solution was stirred at 60 °C for 2 h. To the resulting solution was added dropwise under stirring a solution of bis(2-chloroethyl) ether (1.97 mL, 0.017 mol) in dry DMF (10 mL). The mixture was allowed to stir for 18 h at 60 °C, cooled, and treated cautiously with H<sub>2</sub>O (18

mL) to decompose excess NaH. The solvents were then evaporated under reduced pressure. The residue was extracted with ethyl acetate (4 x 50 mL), washed with of 10% NaOH (2 x 35 mL), H<sub>2</sub>O (2 x 35 mL), and then dried over MgSO<sub>4</sub>. The solvent was evaporated to give a tan solid (3.96 g, 90%), which was crystallized from ethyl acetate to give bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether as white needles (3.54 g, 80%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K): δ 2.14 (6 H, s), 2.18 (6 H, s), 3.69 (4 H, t, *J* = 5.84 Hz), 4.02 (4 H, t, *J* = 5.87 Hz), 5.72 (2H, s). <sup>13</sup>C NMR: δ 10.94, 13.46, 48.36, 70.27, 104.76, 139.62, 147.54.

**Bis[2-(3-phenyl-1-pyrazolyl)ethyl]ether.**<sup>99</sup>



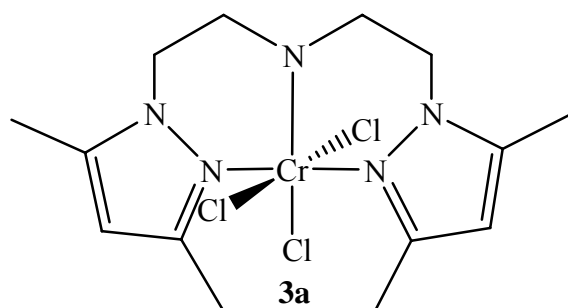
Under an argon atmosphere, 3-phenylpyrazole (4.06 g, 0.028 mol) was slowly added to a suspension of NaH (1.02 g, 0.042 mol) in dry DMF (30 mL) and dry THF (20 mL). The solution was stirred at 60 °C for 2 h. To the resulting solution was added dropwise under stirring a solution of bis(2-chloroethyl) ether (1.69 mL, 0.014 mol) in dry DMF (10 mL). The mixture was allowed to stir for 18 h at 60 °C, cooled, and treated cautiously with H<sub>2</sub>O (15 mL) to decompose excess NaH. The solvents were then evaporated under reduced pressure.

The residue was extracted with ethyl acetate (4 x 40 mL), washed with of 10% NaOH (2 x 30 mL), H<sub>2</sub>O (2 x 30 mL), and then dried over MgSO<sub>4</sub>. The solvent was evaporated to give a tan solid (4.31 g, 86 %), which was crystallized from ethyl acetate to give bis[2-(3-phenyl-1-pyrazolyl)ethyl]ether as white needles (3.91 g, 78%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K): δ 3.79 (4 H, t, *J* = 4.88 Hz), 4.26 (4 H, t, *J* = 4.92 Hz), 6.45 (2 H, s), 7.32 (8 H, m), 7.75 (4 H, m).

### III.3.2 Complexes of Cr (III):

All chromium complexes were prepared following the same experimental procedure as described below.<sup>85a</sup>

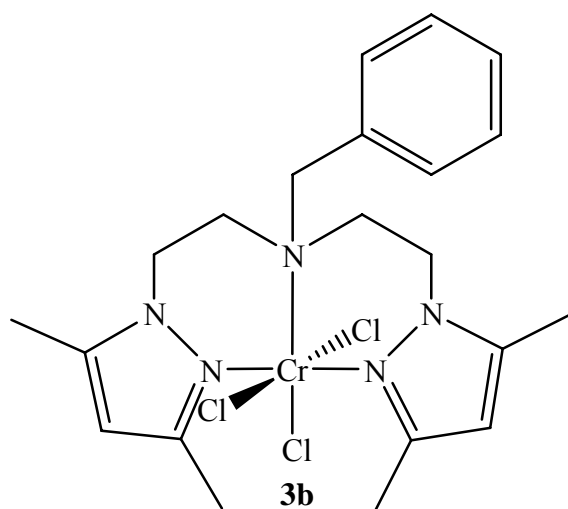
#### [bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine]chromium(III)chloride (**3a**):



Under an argon atmosphere, one solution of bis[2-(3,5 dimethyl-1-pyrazolyl)ethyl]amine (41.8 mg, 0.16 mmol) in THF (10 mL) was added to a solution of CrCl<sub>3</sub>(THF)<sub>3</sub> (54.9 mg, 0.14 mmol) in THF (15 mL). This mixture was allowed to stir for 30 min at room temperature, the solvent was evaporated at ca. 1/3 and pentane (8 mL) was added to this mixture. The title compound precipitates and the solvents were removed by canula. The compound was dried under reduced pressure to give **3** as a green solid (52.8 mg, 89%). Anal. Calc. for

$C_{14}H_{22}N_5Cl_3Cr$  (%) C, 40.16; H, 5.30; N, 16.73; Found (%): C, 39.88; H, 5.56; N, 16.44; ESI-HRMS: 347.0972  $[M-2Cl]^+$  (Calc. for  $C_{14}H_{22}N_5ClCr$  347.0969); IR (KBr,  $cm^{-1}$ ): 2341, 2359 (C=N, pyrazolyl).

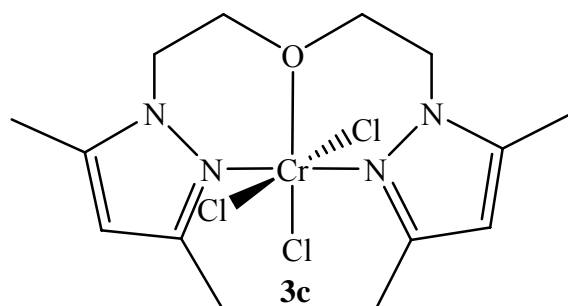
**[bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]benzylamine]chromium(III)chloride (3b):**



A solution of bis[2-(3,5 dimethyl-1-pyrazolyl)ethyl]benzylamine (85.2 mg, 0.24 mmol) in THF (15 mL) was added in one solution of  $CrCl_3(THF)_3$  (83.2 mg, 0.22 mmol) in THF (25 mL). The complex **4** was recovered as a green solid (112 mg, 92%). ESI-HRMS: 473.1171  $[M-Cl]^+$  (Calc. for  $C_{21}H_{29}N_5Cl_2Cr$   $C_{14}H_{22}N_5ClCr$  473.1189).

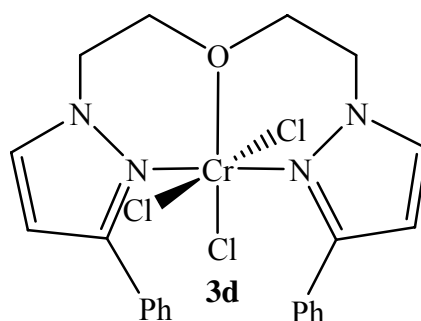


**[bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether]chromium(III)chloride (3c):**



One solution of bis[2-(3,5 dimethyl-1-pyrazolyl)ethyl] ether (77.5 mg, 0.29 mmol) in THF (18 mL) was added in one solution of  $\text{Cr}(\text{THF})_3\text{Cl}_3$  (101.5 mg, 0.26 mmols) in THF (25 mL). The complex **5** was recovered as a red wine solid (98.4 mg, 90%). Anal. Calc. for  $\text{C}_{14}\text{H}_{22}\text{N}_4\text{OCl}_3\text{Cr}$  (%) C, 39.97; H, 5.27; N, 13.32; Found (%): C, 36.96\*; H, 5.65\*; N, 11.49\* (\* This analysis was carried out of the glovebox.); ESI-HRMS: 384.0554  $[\text{M}-\text{Cl}]^+$  (Calc. for  $\text{C}_{14}\text{H}_{22}\text{N}_4\text{OCl}_2\text{Cr}$  384.0577). IR (KBr,  $\text{cm}^{-1}$ ): 2355, 2362 (C=N, pyrazolyl).

**[bis[2-(3-phenyl-1-pyrazolyl)ethyl]ether]chromium(III)chloride (3d):**



One solution of bis[2-(3-phenyl-1-pyrazolyl)ethyl]ether (154.7 mg, 0.43 mmol) in THF (15 mL) was added in one solution of  $\text{Cr}(\text{THF})_3\text{Cl}_3$  (148.1 mg, 0.39 mmols) in THF (20 mL). The complex **6** was recovered as a red wine solid (175.3 mg, 87%). Anal. Calc. for

C<sub>22</sub>H<sub>22</sub>N<sub>4</sub>OCl<sub>3</sub>Cr (%) C, 51.13; H, 4.29; N, 10.84; Found (%): C, 48.99\*; H, 5.48\*; N, 9.26\*  
(\* This analysis was carried out of the glovebox.).

### III.4 Characterization of the supported catalysts

#### III.4.1 X-Ray Fluorescence Spectroscopy

The metal contents on the resulting supported catalysts were determined by X-ray fluorescence spectroscopy (XRF) using a Rigaku (RIX 3100) wavelength dispersive XRF spectrometer tube operated at 50 kV and 70 mA, bearing a LiF 200 crystal and a scintillation counter. Samples were pressed as homogeneous tablets of the compressed (12 MPa) powder of the catalyst systems.

### III.5 Polymerization reactions

The polymerization reactions were performed in 300 mL of hexane/toluene in a 1L Pyrex glass reactor (**Reactor (a)**, Figure III.1) connected to a constant temperature circulator and equipped with mechanical stirring and inlets for argon and the monomer (ethylene). It was added in the reactor a solution of hexane with TMA (trimethylaluminium) (3.0 mL) to remove the impurities, like traces of water and others impurities of the reaction. After 30 minutes, 300 mL of the dry solvent (hexane or toluene) was added. After the thermal stabilization the cocatalyst was added (MAO, TMA or TiBA). The polymerizations were performed at atmospheric pressure of ethylene at 0, 30 and 50°C temperature for 1 h. Acidified (HCl) ethanol was used to interrupt the process, and the reaction products were separated by filtration, washed with distilled water, and finally dried under reduced pressure at 60°C.

In the case of the *in situ* heterogeneization and polymerization reactions, all polymerization reactions were performed in Fisher-Porter bottle (100 mL) (**Reactor (b)**, Figure III.1) equipped with a magnetic stirrer bar and a stainless steel pressure head fitted with inlet and outlet needle valves, a septum-capped ball valve for injections, and a pressure gauge. Under ethylene atmosphere, the appropriate amounts of toluene and **S2** were introduced sequentially. After complete thermal equilibration, the catalyst precursor (**1** and/or **2**) corresponding to 0.1 wt.% transition metal/support was added as toluene solution with stirring. The slurry suspension was stirred for 30 min and then the polymerization reaction was started by the addition of external MAO. For the polymerization reactions using a combination of **1** and **2** we have adopted a general procedure where, initially, a pre-contact reaction between the first catalyst precursor and S2 was carried out for 30 min and then the second catalyst was added, allowing the pre-contact reaction to proceed for an additional 30 min. The polymerization reactions were started by adding external cocatalyst solution to the reactor. The volume of the reaction mixture was 60 mL for all polymerization runs. The total pressure (3 atm) was kept constant by a continuous feed of ethylene. The polymerization runs were stopped introducing 1 mL of methanol.

In the case of the oligomerization reactions, at high pressure of the ethylene, these were performed in a 250 ml double-walled stainless steel reactor (**Reactor (c)**, Figure III.1) equipped with mechanical stirring and continuous feed of ethylene (for reactions using ethylene pressure until 20 atm) and the temperature was controlled by a thermostatic circulation bath. A typical reaction run was performed by introducing in the reactor, under argon, the quantities the alkylaluminum cocatalyst and solvent. The system was saturated with ethylene and the oligomerization reaction was started by introduction of the proper amount of the complex dissolved in 10 mL of toluene. Ethylene was continuously fed in order to maintain the ethylene pressure at the desired value. After 15min, the reaction was stopped

by cooling the system at  $-20^{\circ}\text{C}$  and depressurization. The solution was prepared to injection in the gas chromatographic analysis. After the analysis was added 1 ml of ethanol/HCl to precipitate the polymer.

In all cases, the polymers were washed with acidic ethanol, then ethanol and water, and dried in a vacuum oven at  $60^{\circ}\text{C}$  for 12 h. On the basis of the results of multiple runs, we estimate the accuracy of the activity numbers to be 8%.

### **III.6 Characterization of the polymers and oligomers**

#### **III.6.1 *Differential Scanning Calorimetry***

Polymer melting points ( $T_m$ ) and crystallinities ( $\chi_c$ ) were determined in a Thermal Analysis Instruments DSC-2010 calibrated with Indium, using a heating rate of  $10^{\circ}\text{C}\cdot\text{min}^{-1}$  in the temperature range  $40\text{-}180^{\circ}\text{C}$ . The heating cycle was performed twice, but only the results of the second cycle are reported, since the former is influenced by the mechanical and thermal history of the samples.

#### **III.6.2 *Gel Permeation Chromatography***

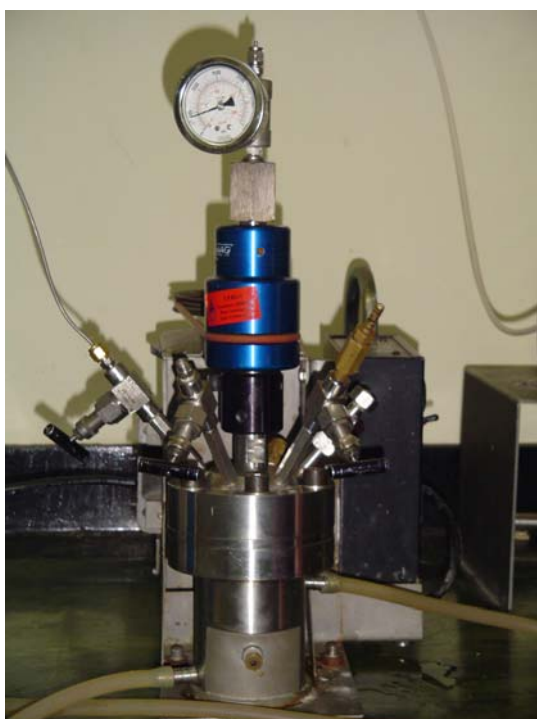
Molecular weight ( $M_w$ ) was evaluated by high-temperature gel permeation chromatography (GPC) with a 150CV, equipped with 3 columns Styragel (103, 104, and 106) working to  $140^{\circ}\text{C}$ , with refractive index and viscosity detectors. Analyses were undertaken using 1,2,4-trichlorobenzene solvent (with  $0.5\text{ g N L}^{-1}$  of Irganox 10/10 as antioxidant).  $M_w$  distributions were calculated using a universal calibration curve built with polystyrene standards.



**Reactor (a):** Glass reactor (1 L) of continuous flow.



**Reactor (b):** Glass reactor (60 mL) Fischer-Porter.



**Reactor (c):** Stainless steel reactor (250 mL) double-walled

**Figure III.1. Reactors used in the polymerization reactions.**

### **III.6.3 Nuclear Magnetic Resonance**

The analysis of  $^{13}\text{C}$  NMR spectroscopy were obtained in a spectrometer Varian it Innovates 300 operating at 75 MHz, at 80 or 120°C, with 71.7° flip angle, acquisition time of 1.5 s and delay of 4,0 s. Sample solutions of the polymer were prepared in *o*-dichlorobenzene and posterior addition of benzene- $\text{d}^6$  (10% w/v) using tubes of 5-mm.

### **III.6.4 Intrinsic Viscosities**

Intrinsic viscosities were determined with an Ubbelohde type viscometer using decalin as solvent at 135°C with a concentration of 0.1 dL/g. The weight molar viscosimetric is calculated leaving of the experimental intrinsic viscosity  $[\eta]$ , the agreement with the following formula  $[\eta] = k(\overline{M}_v)^\alpha$  for  $k = 6,7 \times 10^{-4}$  dL/g and  $\alpha = 0,67$ .<sup>50d,101</sup>

### **III.6.5 Scanning Electronic Microscopy**

SEM micrographs of the supported catalyst systems and polymers were made using a Scanning Electron Microscope (JEOL JSM 5800). For the blend morphology studies, the samples were fractured under liquid nitrogen and the fractured surfaces were coated with gold.

### **III.6.6 Gas Chromatographic Analysis**

The gas chromatographic analysis of the reaction products has been done on a Varian 3400CX equipment with a Petrocol HD capillary column (methyl silicone, 100 m long, i.d. 0.25 mm and film thickness of 0.5  $\mu\text{m}$ ) working at 36°C for 15 minutes and then heating at 5 °C.min<sup>-1</sup> until 250°C.

## **IV. RESULTS AND DISCUSSION**

---

#### IV.1 Ni( $\alpha$ -diimine)Cl<sub>2</sub> SUPPORTED ON MAO-MODIFIED SILICA: INFLUENCE OF POLYMERIZATION PARAMETERS ON ACTIVITY AND POLYMER PROPERTIES

In the last years new late transition metal catalysts for the polymerization of olefins have attracted attention in academia and industry. In particular, aryl-substituted  $\alpha$ -diimine nickel(II) complexes in combination with different cocatalysts show remarkably high activities in polymerization of ethylene.<sup>11,39</sup> With these catalysts, the microstructure of the polymers can be varied by changing the bulk of ortho substituents on the aryl rings and by changing pressure or temperature.<sup>10e,102</sup> This combination of high activities and unique polymer structures make the nickel(II) catalysts desirable for applications in commercial polymerization processes. However, in despite of these interesting properties, as most of the existing polymerization plants run slurry or gas-phase processes with heterogeneous catalysts, such homogeneous ones must be impregnated on a support for the application in those processes. Furthermore, the heterogeneization of catalysts is necessary to avoid reactor fouling with finely dispersed polymer crystals, to prevent excessive polymer swelling, and to produce polymer particles of a desired regular morphology. In this context, the immobilization of a soluble Ni( $\alpha$ -diimine)Cl<sub>2</sub> (**1**) ( $\alpha$ -diimine = 1,4-bis(2,6-diisopropylphenyl)-acenaphthenediimine) catalyst on support seems to be extremely important in order to overcome some problems such as the loss of catalytic performance and reduction of molecular weight at elevated polymerization temperatures.



#### IV.1.1 Preparation of the supported catalysts

It is well-known that the number of silanol groups on the silica surface depends on the thermal treatment, varying from ca.  $5.0 \text{ OH}\cdot\text{nm}^{-2}$  ( $110^\circ\text{C}$ ) to  $1.5 \text{ OH}\cdot\text{nm}^{-2}$  ( $450^\circ\text{C}$ ).<sup>103,104,29</sup> In the present study silica was preheated at  $100^\circ\text{C}$  since at this thermal treatment temperature its surface bears a larger number of silanol groups rendering more likely the immobilization of nickel species on the support. Then, the reaction between silica and **1** (1 wt.% Ni/support) was initially performed in toluene at room temperature for 3 h. In this case, the analysis of supported catalysts (**S1**) by XRF showed that the nickel content on the silica was 0.59 wt.% Ni/SiO<sub>2</sub>.

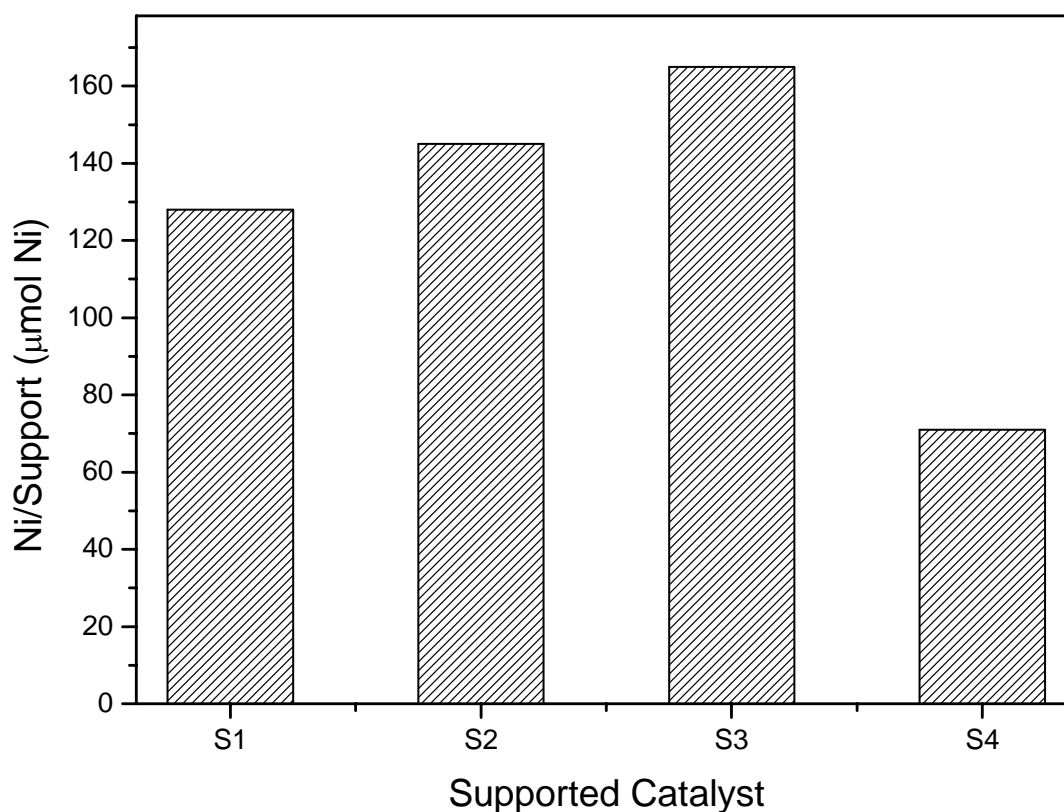
For metallocene catalysts, studies have revealed that the silica chemically modified with MAO allow to impregnate a higher amount of catalytic species on the surface resulting in a more active supported catalysts in comparison with that using bare silica.<sup>105</sup> Taking into account this fact we decided to immobilize the nickel complex on MAO-modified silicas containing 4.0, 8.0 and 23.0 wt.% Al/SiO<sub>2</sub>. The supported catalysts (**S2-S4**) were prepared by reaction of **1** (1 wt.% Ni/support) with MAO-modified silica in toluene at room temperature for 3 h. Table IV.1 shows the resulting nickel content determined by XRF expressed in terms of wt.% Ni/SiO<sub>2</sub>. The nickel content on the MAO-modified silicas varied from 0.31 to 0.81 wt.% Ni/support, being the highest value attained for the MAO-modified silica containing 8.0 wt.% Al/SiO<sub>2</sub>.

The Figure IV.1 shows the dependence of the nickel amount on the Al content present on the silica surface. Comparing nickel contents among **S1-S3** systems, it was observed that as the Al content increases, from 0.0 to 8.0 wt.% Al/SiO<sub>2</sub>, more nickel species are adsorbed on the support suggesting that **1** bound preferably to the MAO present on the surface. According to Table IV.1, in the case of commercial MAO-modified silica, in spite of bearing higher Al content, lower grafted Ni species was observed. Similar results were reported for

grafted  $(n\text{BuCp})_2\text{ZrCl}_2$ ,<sup>106</sup> and  $\text{Tp}^{\text{Ms}^*}\text{TiCl}_3$ <sup>34</sup> in which lower metal content was observed in the case of MAO-modified commercial silica in comparison to those results noticed for silica modified with lower Al contents.

**Table IV.1** Resulting Ni content in the supported catalysts.

System	Support	$\mu\text{mol Ni/support}$	wt.% Ni/support
<b>1/S1</b>	$\text{SiO}_2$	128	0.59
<b>1/S2</b>	$\text{SiO}_2/\text{MAO}(4\%)$	145	0.70
<b>1/S3</b>	$\text{SiO}_2/\text{MAO}(8\%)$	165	0.81
<b>1/S4 (commercial)</b>	$\text{SiO}_2/\text{MAO}(23\%)$	71	0.31



**Figure IV.1** Correlation between nature of the support and Ni content (wt.%).

### IV.1.2 Ethylene polymerization using the supported catalysts S1-S4

In order to verify the influence of Al content on the support to the activity, some polymerization reactions were performed at 30°C, in toluene and using a molar ratio Al/Ni = 1000. The results are presented in the Table IV.2.

**Table IV.2:** Ethylene polymerization, using the catalytic precursor **1** immobilized in silica and MAO-modified silica.<sup>a</sup>

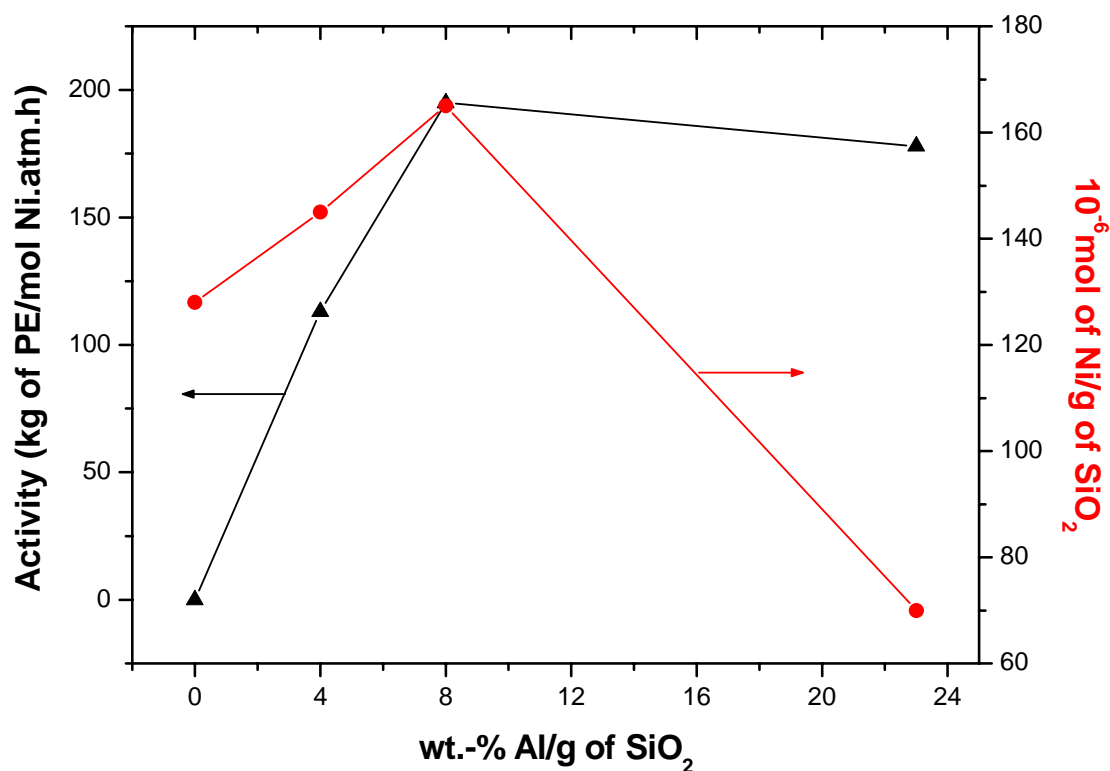
Entry	Support	Cat. ( $\mu\text{mol}$ )	Polymer (g)	Activity <sup>c</sup>	Mw (g/mol) $\times 10^{-3}$	Mw/Mn
1	<b>S1</b>	3.62	-	-	-	-
2	<b>S2</b>	3.74	0.42	113	362	7
3	<b>S3</b>	3.71	0.73	196	413	1.7
4	<b>S4</b>	3.62	0.64	177	332	1.9
5	<b>Homogeneous</b>	5.00	5.15	2100	180	2.0

Polymerization Conditions: <sup>a</sup> Glass reactor (1L); toluene (350 mL), Al/Ni = 1000, 30°C, 60 min, atmospheric pressure of ethylene; <sup>b</sup> Glass reactor (1L); toluene (350 mL), Al/Ni = 1095, 30°C, 30 min, atmospheric pressure of ethylene <sup>c</sup> Kg of PE/mol[Ni].h.atm.

All the supported systems were shown to be active in ethylene polymerization with exception of **S1**. The non-activity of supported catalyst **S1** can be probably attributed to the formation of inactive catalytic species. In this case, we could suggest that the nickel compound **1** reacts with hydroxyl on silica surface to form a stable  $\text{Si}-\{\text{DAD}\}\text{Ni}(\text{O}-\text{Si}\equiv)_x\text{Cl}_y$  compound which is not converted to a catalytic species upon reacting with external cocatalyst.

The supported catalysts **S2-S4** displayed activity varying from 113 to 196 kg of PE/mol[Ni].h.atm. In addition, higher activity was obtained using the supported catalysts **S3** containing 8.0 wt.% Al/SiO<sub>2</sub> (entry 3, 196 kg of PE/mol[Ni].h.atm). Catalysts prepared with supports containing more than 8.0 wt.% Al/SiO<sub>2</sub> showed similar activity. For instance, the

activity found for **S4** which contain 23.0 wt.% Al/SiO<sub>2</sub> is 177 kg of PE/mol[Ni].h.atm). It should be pointed out that the Ni content in **S4** is lower than **S3** suggesting that the presence of higher amount of Al on the support determines a better distribution of the Ni metal on the surface affording higher amount of the species actives. This observation is better visualized correlating the Ni contents and type of supports with the activities as shown in Figure IV.2.



**Figure IV.2.** Correlation between the activity, wt.% Al/SiO<sub>2</sub> and the  $\chi_{Ni}$  immobilized in the silica modified with MAO in the polymerization reactions for 30°C, in toluene and using a molar ratio Al/Ni = 1000.

Comparing the performance of the homogeneous system with the supported ones, a reduction in the activity is clearly observed in the latter cases. For instance, the most active supported system **S3** (196 kg of PE/mol[Ni].h.atm) is 11 times less active than the

homogeneous (2100 kg of PE/mol[Ni].h.atm). This reduction might be due to the decreasing of the number of active species generated on the support surface. Similar results have been reported in the case of supported zirconocenes, where only ca. 1% of the supported species are believed to be active.<sup>107</sup>

The polymer properties have been evaluated by means of differential scanning calorimetry (DSC), and Gel Permeation Chromatography (GPC). Characteristics of the resulting polymers are shown in Table IV.2. The polymers produced by the supported catalysts showed the absence of melting temperature peaks in the DSC curves indicating the formation branched polyethylenes. In this case the immobilization of **1** on the surface of the MAO-modified silica is not enough to produce more crystalline polymers if compared with the homogeneous system. On the other hand, the influence of the support on the molecular weight (Mw) of the polyethylenes is clear considering that the supported catalysts (**S2-S4**) produce PE with higher molecular weight than that one presented by the Ni homogenous. For instance, the PE's produced by **S2-S4** presented Mw in the range of 332.000-413.000 g/mol while that one produce by Ni homogeneous showed Mw of 180.000 g/mol. The higher Mw obtained with the supported catalysts can be attributed to a decrease of  $\beta$ -hydride elimination rate.<sup>39b</sup>

It should be pointed out that, in all cases the GPC curves displayed monomodal molecular weight distributions (MwD's) with polydispersities varying from 1.7 to 7.0. The broad MwD obtained using **S2** can be assigned to the formation of at least two different active species on the support. It is not clear at this moment the reason why the supported catalysts **S3** and **S4** showed different behavior related to **S2**.

### IV.1.3 Effects of the polymerization conditions using the supported catalyst S2

Based on the preliminary ethylene polymerization studies involving the supported catalysts **S1-S4**, we decided to carry out some additional studies using **S2** in order to evaluate the influence of some polymerization parameters namely solvent, temperature, Al:Ni molar ratio, and nature of cocatalyst on the activity and the polymer properties..

The ethylene polymerization reactions were carried out using MAO-activated system with **S2** in hexane/toluene at 0, 30, and 50°C. The Table IV.3 shows the polymerization results by varying the Al/Ni molar ratio from 200 to 2000.

**Table IV.3.** Ethylene polymerization using **S2**.<sup>a</sup>

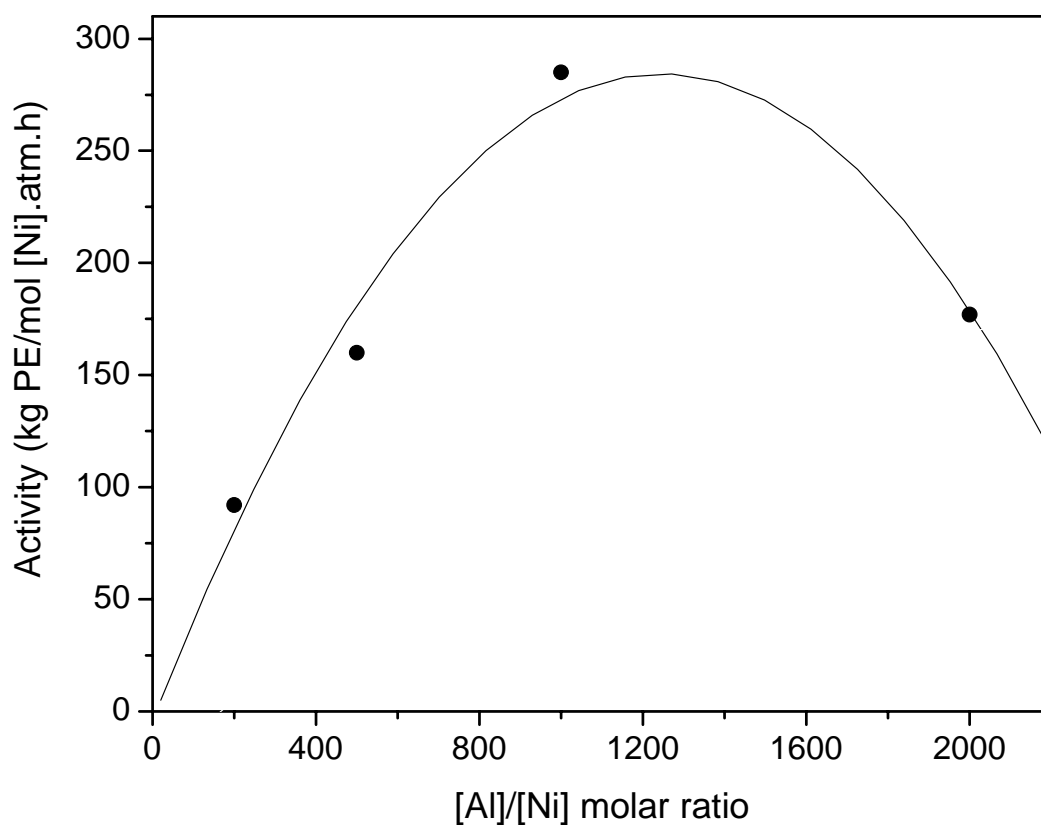
Entry	Solvent	Al/Ni Ratio	Temp. (°C)	Polymer (g)	Activity <sup>d</sup>	Tm (°C)	$\chi$ (%)	Mw (g/mol)x10 <sup>-3</sup>	Mw/Mn
6	Hexane	200	30	0.34	92	-	-	283	10
7	Hexane	500	30	0.59	161	-	-	293	7
8	Hexane	1000	0	0.45	125	119	24	752	1.9
9	Hexane	1000	30	0.94	285	-	-	194	6
10	Hexane	1000	50	0.55	149	-	-	134	1.6
11	Hexane	2000	30	0.56	177	-	-	311	11
12	Toluene	1000	30	0.42	112	-	-	362	7

Polymerization Conditions: *a* Glass reactor (1L); approximately 3.62  $\mu\text{mol}$  of Ni; MAO as cocatalyst; 60 min; atmospheric pressure of ethylene, *b* reactor of steel inox (75 mL); pressure of ethylene of 30 atm, for 5 minutes; *c* **1** homogeneous, reactor of steel inox (75 mL); pressure of ethylene of 30 atm, for 5 minutes; *d* kg of PE/mol[Ni]·atm·h.

To get an initial survey of the polymerization activity of **S2** the ethylene polymerizations have been investigated in hexane and toluene at 30°C and using the molar ratio  $[\text{Al}]/[\text{Ni}] = 1000$ . Higher activity was obtained using hexane as solvent (Table IV.3, entry 9 vs 12). The available data for this catalytic system are very limited at present,

however, based on the studies performed by McConville et al. related to non-metallocene titanium compounds,<sup>108</sup> we speculate that the lower activity of this catalytic specie in toluene could be associated to the coordination capacity of toluene to nickel, which might engender a competition between the coordinating olefin and the solvent itself.

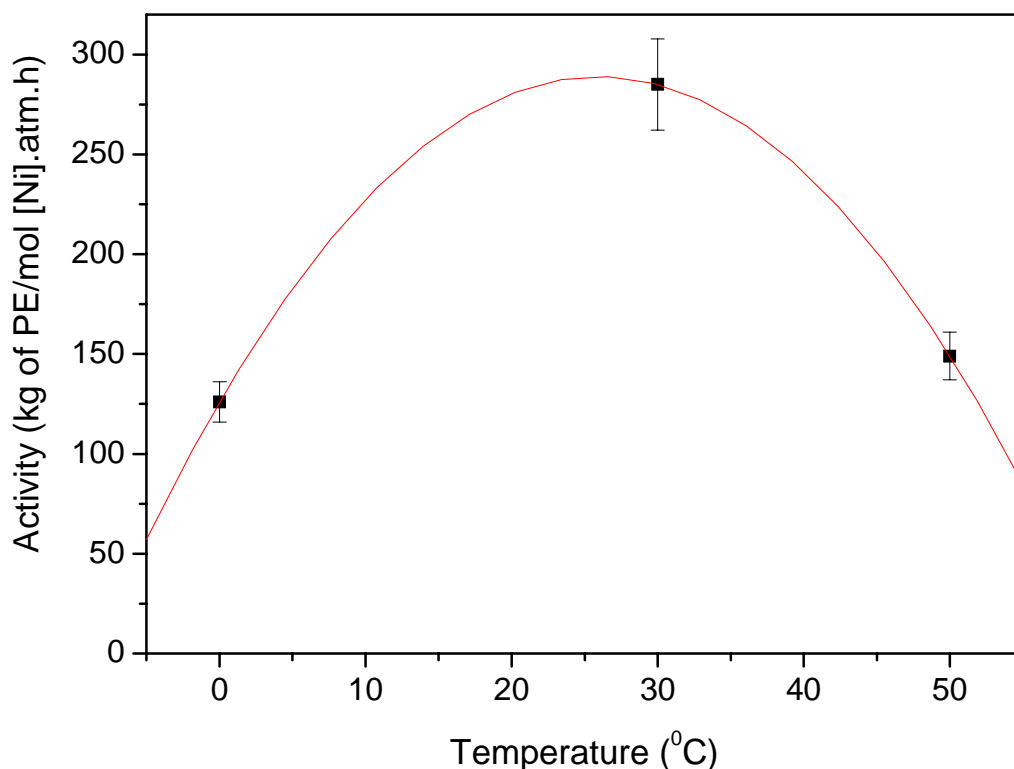
Considering the higher activity of **S2** in hexane, an additional study was carried out aiming at evaluating the influence of the [Al]/[Ni] molar ratio on activity. One set of experiment was performed using hexane as solvent at 30°C, utilizing MAO as activator system. As can be observed in Figure IV.3, the use of low concentrations of Al determines the formation of active catalytic species. Polymerization runs varying the [Al]/[Ni] molar ratio from 200:1 to 2000:1 revealed that the system is active at [Al]/[Ni] molar ratio as low as 200:1 (entry 5, 92 kg of PE/mol[Ni].h.atm). Maximum activity was attained using [Al]/[Ni] molar ratio of 1000:1 (entry 8, 285 kg of PE/mol[Ni].h.atm). Increasing the Al concentration to 2000 resulted in lower activity (entry 10, 177 kg of PE/mol[Ni].h.atm.) According to these results, the optimum Al concentration required to obtain an excellent performance of the nickel catalyst has been found using 1000:1.



**Figure IV.3.** Effect of the ratio Al/Ni about the catalytic activity for the system **S2**.

In general, the influence of the polymerization temperature on activity of **S2** demonstrates a significant increase of the polymerization conversion by an enhancement of the temperature from 0 to 30°C as a consequence of higher solubility of the activator at this temperature (30°C) (Figure IV.4). A further increase to 50°C leads to a decrease of the polymerization conversion, indicating a reduced complex stability. Similar results have been found for Ni catalyst in homogeneous medium.<sup>109</sup>





**Figure IV.4.** Effect of the temperature in the catalytic activity of the system **S2**.

As expected, the GPC results showed that the use of different  $[Al]/[Ni]$  molar ratios do not influence the  $M_w$  of the PE's taking into account that the main chain-transfer pathway using Ni catalysts is through  $\beta$ -H transfer to metal. For the polymerization reactions varying the temperature, it was observed a significant reduction of the  $M_w$  as the polymerization temperature increase [from 752.000 at 0°C to 134.000 at 50°C]. This reduction is associated to higher  $\beta$ -H elimination rate at higher polymerization temperature.

The DSC curves of the polyethylene's produced at 30 and 50°C do not show melting peaks as results of the formation of branch PE. On the other hand, the PE produced at 0°C was found to exhibit melt transition ( $T_m$ ) of 119°C.

To investigate the effects of the ethylene pressure on activity and polymer properties, polymerizations of ethylene were performed with catalyst precursor **S2** in toluene and hexane at 60°C, and using [Al]/[Ni] molar ratio of 1000. Representative data for ethylene polymerizations are summarized in Table IV.4.

Similarly found for the polymerization runs at low pressure, higher activity was obtained in hexane (compare entry 13 vs 15). Furthermore, it was observed that the polymerization reactions using **1** in homogeneous medium showed higher activities related to the supported catalysts. As mentioned before, this reduction can be associated to the decreasing of the number of active species generated on the support surface.

Polyethylenes produced by **S2** were firstly characterized by differential scanning calorimetry (DSC). DSC curves of the PE produced by the supported catalyst showed  $T_m$  in the range from 90 to 114°C. In general, these values are higher than those ones obtained using Ni homogeneous (entry 14, hexane, 109°C; entry 16, toluene, 64°C) indicating that the immobilization of **1** on the support provokes the formation of more crystalline PE. Exceptionally, the DSC curve of the PE produced by **S2** in hexane (entry 13) shows clearly the appearance of two peaks in distinct temperature regions suggesting the formation of two different catalyst species in the polymerization medium Figure IV.5.

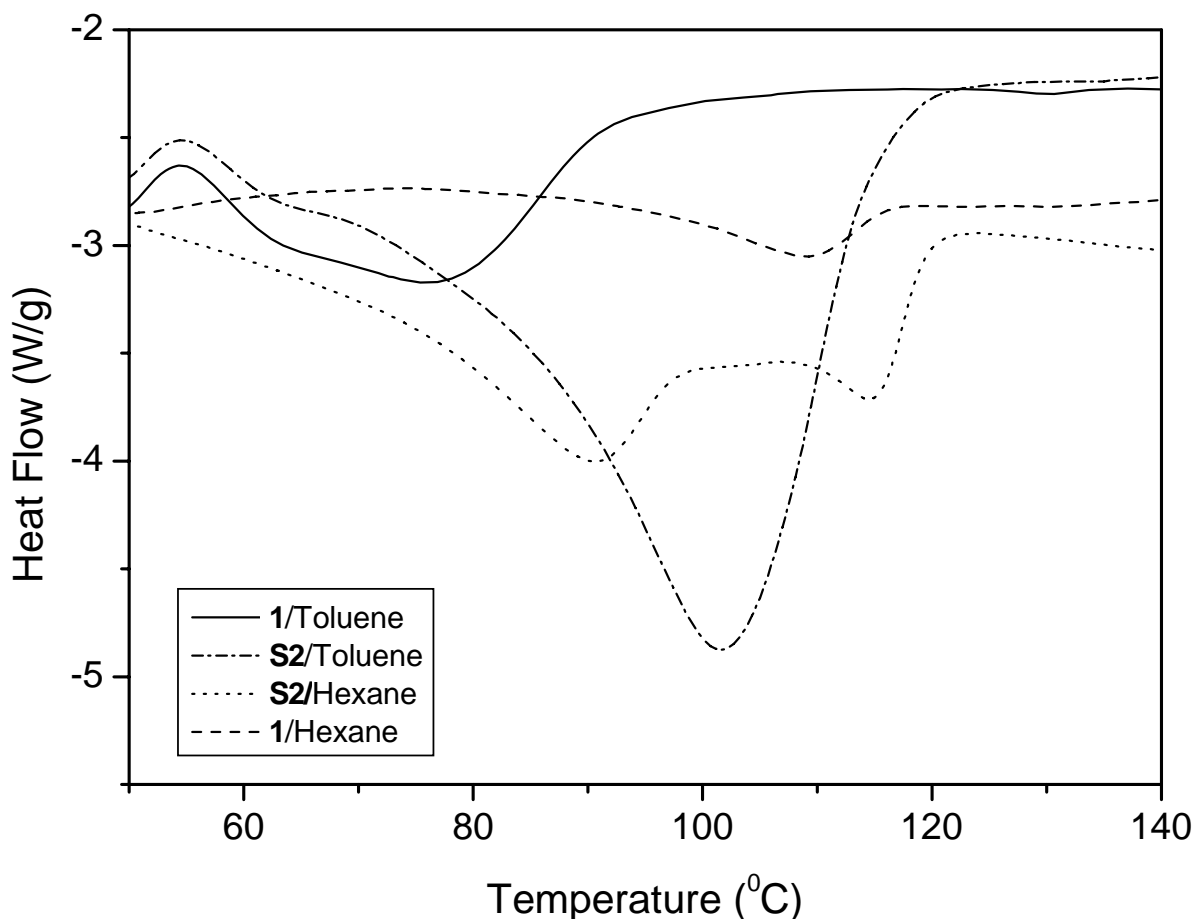
**Table IV.4.** Results of ethylene polymerization at high pressures using the catalytic precursors **1** and **S2**.<sup>a</sup>

Entry	Solvent	Polymer (g)	Activity <sup>d</sup>	T <sub>m</sub> (°C)	χ (%)	M <sub>w</sub> (g/mol)x10 <sup>-3</sup>	M <sub>w</sub> /M <sub>n</sub>
13 <sup>(b)</sup>	Hexane	1.98	219	90 114	8 3	1,052	5.4
14 <sup>(c)</sup>	Hexane	10.40	1149	109	0.6	201	3.5
15 <sup>(b)</sup>	Toluene	1.60	171	101	22	369	2.7
16 <sup>(c)</sup>	Toluene	8.78	970	64	4	510	1.9

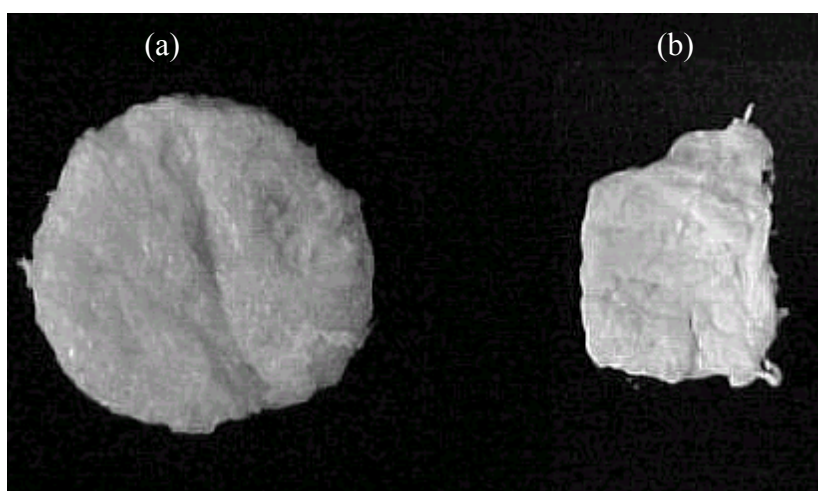
<sup>a</sup> Polymerization Conditions: <sup>b</sup> reactor of steel inox (75 mL); approximately 3.62 μmol of Ni; pressure of ethylene of 30 atm; molar ratio Al/Ni = 1000; MAO as cocatalyst; 60°C for 5 minutes. <sup>c</sup> **1** homogeneous, reactor of steel inox (75 mL); pressure of ethylene of 30 atm, for 5 minutes; <sup>d</sup> kg of PE/mol[Ni].h.atm.

The GPC results show that the M<sub>w</sub> of the polyethylene's produced using **S2** are higher than those ones produced in homogenous medium as consequence of a decrease of β-hydride elimination rate after immobilization of **1** on the support as discussed previously. The effect of the support is more pronounced when we compare the M<sub>w</sub> of the PE produced in hexane where the PE obtained using **S2** (entry 13, 1,052.000 g/mol) is 5 times higher than that one obtained using **1** (entry 14, 201.000 g/mol).

The Figure IV.6 shows the image of the PE's produced at 60°C using 30 atm of ethylene pressure in homogeneous (a) and heterogeneous (b) medium. Comparing both images is evident the formation of more branching PE produced by **1** (rubber-like PE) related to more linear PE produced by **S2**.



**Figure IV.5.** DSC curves of polymers using the catalytic precursors **1** and **S2**. Polymerization Conditions: reactor of steel inox (75 mL); pressure of ethylene of 30 atm, ratio  $[Al]/[Ni] = 1000$  at 60°C for 5 minutes.



**Figure IV.6.** Polyethylene produced using **1** (a) and **S2** (b) (60°C, 30 atm, toluene,  $[Al]/[Ni] = 1000$ ).

Objecting to get some insights related to the influence of cocatalyst type on activity and polymer properties, a preliminary study involving **S2** was performed in toluene at 30°C under ethylene atmosphere pressure. The results are summarized in Table IV.5.

The use of other Lewis acid cocatalysts such as trimethylaluminum (TMA) resulted also in active ethylene polymerization catalyst with activity similar related to achieve using MAO. For instance, the polymerization reaction using MAO showed activity of 11 kg of PE/mol[Ni].h.atm while that employing TMA was 14 kg of PE/mol[Ni].h.atm. It is worth noting that polymerization reaction using only TMA as cocatalyst showed that this resulting supported catalysts is active in the absence of external MAO. Thus, it seems that the MAO present on the support might act as cocatalyst, generating active species during the polymerization reaction. In the polymerization reaction carried out using triisobutylaluminum (TiBA) no production of polyethylene has been observed.

**Table IV.5.** Ethylene polymerizations with different cocatalyst using the system **S2**.<sup>a</sup>

Entry	Cocatalyst	Polymer (g)	Activity <sup>b</sup>	Mw (g/mol)x10 <sup>-3</sup>	Mw/Mn
17	MAO	0.04	11	165	6
18	TMA	0.05	14	533	1.9
19	TiBA	-	-	-	-

<sup>a</sup> Polymerization Conditions: Glass reactor (1L); approximately 3.62 μmol of Ni; 60 min; atmospheric pressure of ethylene; molar ratio Al/Ni = 200; 30°C. <sup>b</sup> kg of PE/mol[Ni]·atm·h

DSC results show the absence of melting peak as consequence of the formation of branch PE. The GPC results showed that the molecular weight of the polyethylene depends on alkylaluminum type, increasing from MAO to TMA. Furthermore, it was observed that the use of TMA instead of MAO provokes a narrowing of the polydispersity suggesting that the use of the former cocatalyst generates only one active species on the support.

#### IV.1.4 “*In situ*” heterogeneization of NiDADCl<sub>2</sub> on MAO-modified silica

The polymerization reactions using supported catalysts are time demanding, involving reaction and washing steps and final catalyst characterization. Soares et al. proposed an alternative methodology (*in situ* supporting) which uses an immobilized cocatalyst.<sup>53</sup> This approach consists in the direct addition of the catalyst solution to the MAO-supported silica inside the reactor, just before pressurizing with monomer. Furthermore, UV-visible studies performed by Deffieux,<sup>110</sup> using ( $\alpha$ -diimine)NiBr<sub>2</sub>/MAO catalyst system, showed that this system is not stable in absence of olefin. In this context, considering the instability of the catalytic species formed by interaction Ni( $\alpha$ -diimine)Cl<sub>2</sub> (**1**) and MAO in the absence of monomer, we decided to perform some polymerization reactions using supported catalyst generated *in situ* by reacting directly in the reactor 1 with MAO-modified silica containing 4.0 wt.% Al/SiO<sub>2</sub> under ethylene atmosphere.

Studies employing the catalytic precursors **1** and *in situ* ethylene polymerization reactions were performed by established pre-contact of **1** with **S2** for 30 min (vide experimental section) determining the formation of catalytic system namely **1/S2**. All ethylene polymerization reactions were carried out using an amount of catalyst precursors **1** corresponding to 0.10 wt.% Ni/support. Table IV.6 shows the results of polymerization runs.

The polymerization reactions using *in situ* supported catalyst carried out in hexane or toluene exhibited activities of 201 and 603 kg of PE/mol[Ni].h.atm respectively. These values are two times higher than that displayed using the supported catalyst **S2** taking into account the solvent utilized in the polymerization reaction (113 and 285 kg of PE/mol[Ni].h.atm). These data are in accord with the UV/VIS spectroscopy results<sup>110</sup> suggesting that the most part of the nickel species are deactivated during the grafting process after reaction with MAO. Similar results have been observed for another non metallocene complexes supported on MAO-modified silica.<sup>111</sup>

**Table IV.6.** Ethylene polymerization results using Ni(diimine- $\alpha$ )Cl<sub>2</sub> (**1**) catalyst supported *in situ* on S2.<sup>a</sup>

Entry	Solvent	S2 (g)	Polymer (g)	Activity <sup>b</sup>	Mw (g/mol)x10 <sup>-3</sup>	Mw/Mn
20	Toluene <sup>c</sup>	0.253	0.42	113	362	7
21	Toluene <sup>d</sup>	0.251	0.75	201	290	2.2
9	Hexane <sup>c</sup>	0.250	0.94	285	194	6
22	Hexane <sup>d</sup>	0.252	2.18	603	482	2.3

<sup>a)</sup> Polymerization conditions: Fischer Porter bottle (100 mL), [Ni] = 2  $\mu$ mol, solvent = 75 mL, [Al]/[Ni] = 1000, P<sub>C<sub>2</sub>H<sub>4</sub></sub> = 3.0 atm, 30°C, polymerization time = 1h, MAO as external cocatalyst, pre contact of **1** with SMAO for 30 min; <sup>b)</sup> kg of PE/mol[Ni]·h·atm; <sup>c)</sup> polymerization reactions using **S2**; <sup>d)</sup> Polymerization reactions using *in situ* supported nickel catalyst.

The resulting polyethylenes were characterized by DSC and GPC. The DSC results show the absence of melting peak indicating, in all case, the formation of branched PE. The Mw of the PE produced in toluene via *in situ* supported catalyst is very similar to those obtained using **S2**. On the other hand, the polymers produced in hexane via *in situ* supported catalyst exhibited higher Mw than those obtained with **S2**. In this case, the Mw increases 2.5 time using *in situ* supported catalyst (entry 9, 194.000 g/mol; entry 22, 482.000 g/mol). It is interesting to note that the MwD become narrow using the *in situ* polymerization process with polydispersities around 2.0 suggesting that this process generates only one active specie on the support.

## IV.2 ETHYLENE POLYMERIZATION USING COMBINED Ni AND Ti CATALYSTS SUPPORTED IN SITU ON MAO-MODIFIED SILICA

A large range of polyolefinic materials with interesting properties have been disclosed in the last decades as a result of the development of new classes of olefin polymerization catalysts<sup>42a,112</sup> as well as of blending existing polymers.<sup>113</sup> Furthermore, a new approach has been introduced that is based on catalyst systems that combine, in a single reactor, two or more types of catalysts that produce polymers with different and controlled molecular weight averages (Mw) and molecular weight distributions (MwD).<sup>114</sup> This method has been successfully used to produce linear low density PE (LLDPE),<sup>115</sup> branched polyethylenes,<sup>116</sup> polyethylenes with long chain branches (LCB-PE),<sup>117</sup> ethylene/1-hexene copolymers,<sup>118</sup> and polyethylene blends<sup>50d</sup>. Furthermore, some binary catalyst systems have been supported onto inorganic supports in order to produce polyethylene with bimodal molecular weight distribution.<sup>119</sup>

In the last few years we have developed homogeneous binary catalyst systems for the production of polyethylene blends<sup>120</sup> and LLDPE<sup>121</sup>. Our studies demonstrated that the variation of polymerization parameters such as solvent, cocatalyst, temperature of polymerization as well as metal mole fraction strongly influences the activity and polymer properties. Particularly, for the binary catalytic system composed of Ni( $\alpha$ -diimine)Cl<sub>2</sub> (**1**) ( $\alpha$ -diimine = 1,4-bis(2,6-diisopropylphenyl)-acenaphthenediimine)/Tp<sup>Ms\*</sup>TiCl<sub>3</sub> (**2**) (Tp<sup>Ms\*</sup> = hydridobis(3-mesitylpyrazol-1-yl)(5-mesitylpyrazol-1-yl))<sup>120a</sup> we have found evidences of synergistic effects between the two catalytic species. Previous studies involving the single supported catalyst precursors Ni( $\alpha$ -diimine)Cl<sub>2</sub><sup>122</sup> and {Tp<sup>Ms\*</sup>}TiCl<sub>3</sub><sup>34</sup> on MAO-modified silica (SMAO) revealed that these systems have low activity for ethylene polymerization because of the instability of the catalytic species formed by interaction of **1-2** and MAO in the



absence of monomer. On the other hand, polymerization carried out using these catalysts supported *in situ* show activities 4-fold higher than those found when they were immobilized on MAO-modified silica.<sup>34</sup>

In the present investigation, we decided to carry out ethylene polymerizations using combined Ni and Ti catalysts supported *in situ* on MAO-treated silica (**S2**) in order to see if the synergistic effects between the Ni and Ti species observed in solution were also present after heterogenization, and also to produce polymer particles of a desired regular morphology. Studies related to the effect of polymerization temperature, immobilization order, and nickel mole fraction ( $x_{Ni}$ )<sup>123</sup> on the activity and polymer properties will be described below.

#### **IV.2.1 Influence of $x_{Ni}$ and polymerization temperature on catalyst activity.**

Before run the polymerizations reactions we made a test to certificate that the all metal (M = Ni + Ti) present on the reactor are immobilized in the silica (**S2**) on the reactions conditions. These are the impregnation of the catalysts (in a Schlenck with atmosphere of ethylene) with  $x_{Ni} = 0.50$  (with 30 min of pre-contact for Ni and for Ti) followed by the filtration of the solution to the polymerization reactor and addition of external MAO. The polymerization was carried out for 1 hour and is not found PE. That indicated that the catalyst **1** and **2** met fixed to the support (**S2**).

The ethylene polymerization reactions using combined Ni and Ti catalysts supported *in situ* on **S2** were performed in toluene at 0 and 30°C adopting the methodology introduced by Soares et al.<sup>53</sup> All ethylene polymerization reactions were carried out using an amount of catalyst precursors **1** and **2** corresponding to 0.10 wt.% M/support (M = [Ni] + [Ti]). This concentration was chosen considering that it is much lower than those found for the isolated Ti and Ni species present on the **S2** determined by X-ray fluorescence spectroscopy (XRF). (0.70 wt.% Ni/support ; 0.80 wt.% Ti/support). Therefore, all the Ni and Ti present in solution

might have immobilization sites available on the support. The Table IV.7 shows the results of polymerization runs for several nickel molar fractions ( $x_{Ni}$ ).

The ethylene polymerization reactions performed at 0°C showed that the *in situ* supported catalyst **1/S2** is more active than **2/S2** as can be seen comparing entries 5 (673 kg of PE/mol[Ni].h.atm) and 1 (430 kg of PE/mol[Ti].h.atm). The polymerization runs carried out at higher temperature (30°C) showed lower activities for both systems (compare entries 6 and 10). The lower activities at these polymerization conditions can be attributed to the lower thermal stability of the catalytic species formed by interaction of **1** and **2** with the MAO-modified silica.

Studies employing the combination of catalytic precursors **1** and **2** and *in situ* ethylene polymerization reactions were performed by established pre-contact of **1** with **S2** for 30 min followed by addition of **2** (vide experimental section) determining the formation of catalytic system namely **2/1/S2**.

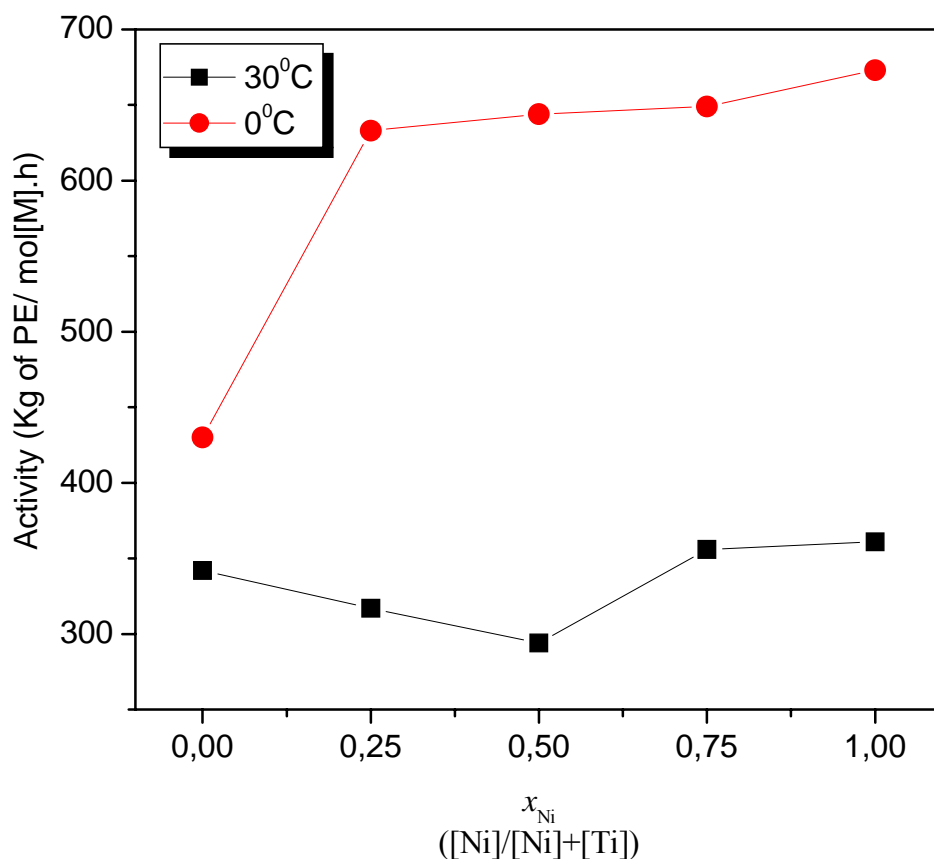
In the polymerization reactions performed at 0°C, it was observed that the activity increased slightly in the presence of a minimum amount of **1** in the polymerization medium ( $x_{Ni} = 0.25$ , 633 kg of PE/mol[M].h.atm) compared to the predicted one (491 kg of PE/mol[M].h.atm).<sup>124</sup> Nevertheless, it is worth pointing out that the presence of a higher concentration of nickel catalyst did not cause a significant increase in activity (Figure IV.7). For instance, the polymerization reactions using  $x_{Ni}$  in the range of 0.50 to 1.00 exhibited similar activities with the values ranging from 644 to 673 kg of PE/(mol[M].h.atm).

**Table IV.7.** Ethylene polymerization results using combined Ni(diimine- $\alpha$ )Cl<sub>2</sub> (**1**) and {Tp<sup>M<sub>S</sub>\*</sup>}TiCl<sub>3</sub> (**2**) catalysts supported in situ on **S2**.<sup>a</sup>

Entry	$x_{Ni}$	S2 (g)	time (min)	T (°C)	Polymer (g)	Activity. <sup>b</sup>	T <sub>m</sub> (°C)	$\chi$ (%)	[ $\eta$ ] (g/dL)
1	0.00	0.1862	10	0	0.43	430	134	18	7.47
2	0.25	0.1824	10	0	0.63	633	127	22	9.22
3	0.50	0.1872	10	0	0.64	644	124	22	5.78
4	0.75	0.1839	10	0	0.65	649	121	24	5.83
5	1.00	0.1887	10	0	0.67	673	119	23	4.81
6	0.00	0.1869	30	30	1.03	342	138	40	7.43
7	0.25	0.1817	30	30	0.95	317	134	34	5.49
8	0.50	0.1850	30	30	0.88	294	134	31	8.83
9	0.75	0.1882	30	30	1.07	356	134	28	6.00
10	1.00	0.1847	30	30	1.08	361	-	-	3.81
11	0.25 <sup>c</sup>	0.1869	10	0	0.66	658	130	24	9.85
12	0.50 <sup>c</sup>	0.1852	10	0	0.62	621	127	20	7.10
13	0.75 <sup>c</sup>	0.1874	10	0	0.69	694	127	22	6.95

<sup>a</sup> Polymerization conditions: Fischer Porter bottle (100 mL), [M] = 2  $\mu$ mol, toluene = 75 mL, [Al]/[M] = 300, P<sub>C<sub>2</sub>H<sub>4</sub></sub> = 3.0 atm, blank MAO runs were carried out every 5 normal runs, MAO as external cocatalyst; <sup>b</sup> kg of PE/mol[M]·h·atm; <sup>c</sup> pre contact of **2** with SMAO followed, after 30 min, by addition of **1**.

At higher temperature (30°C), the activities remained nearly constant as  $x_{Ni}$  increased in the polymerization medium as consequence of the similar activities found for **1/S2** and **2/S2** when used as single catalyst (Figure IV.7). Moreover, no evidence of a synergistic effect between the catalytic species after immobilization on MAO-modified silica could be detected. In this context, we can speculate that the absence of a synergistic effect can be associated to the presence of MAO on the surface that acts as spacer keeping the Ti centers away from the Ni species.



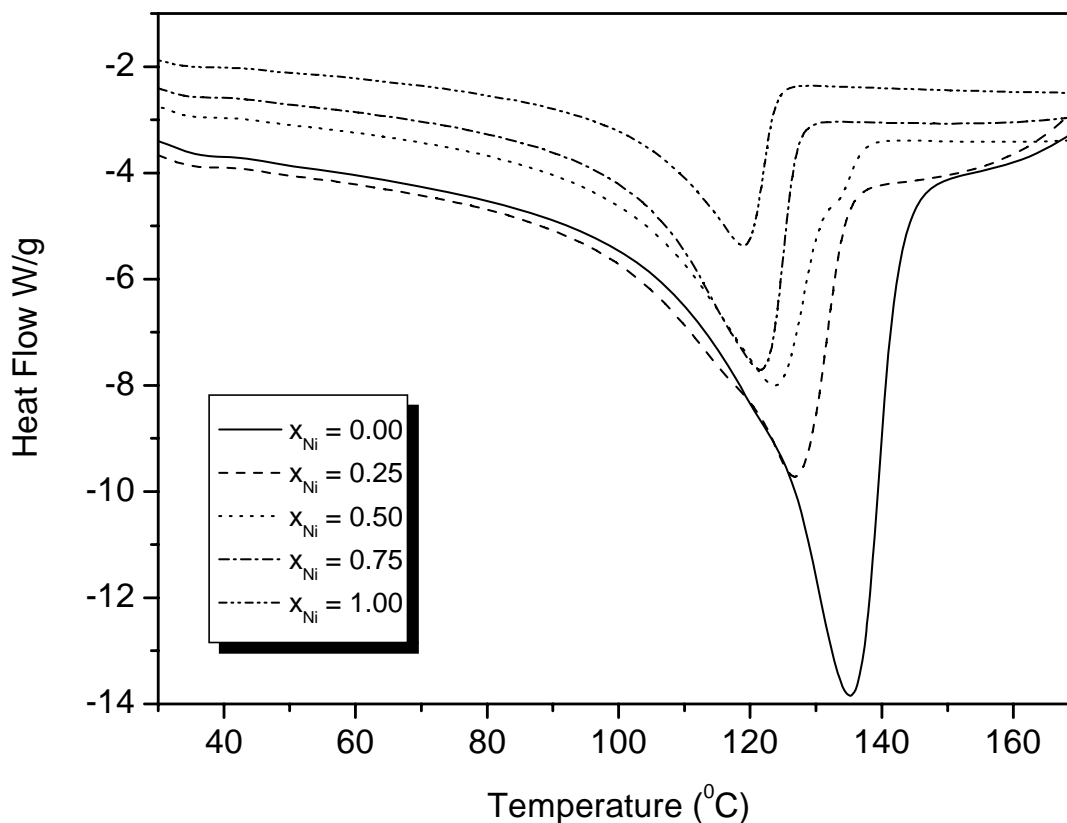
**Figure IV.7.** Influence of polymerization temperature on the activity for **1/2/S2** varying  $x_{Ni}$ .

In order to determine if the immobilization order influences catalyst activity, some additional studies were carried out in which the more sterically demanding catalyst  $Tp^{Ms*}TiCl_3$  (**2**) was initially immobilized onto **S2**, followed by  $Ni(\alpha\text{-diimine})Cl_2$  (**1**) (catalytic system namely **1/2/S2**). For all nickel molar fractions investigated ( $x_{Ni} = 0.25\text{-}0.75$ ), very similar activities were found for **1/2/S2** and **2/1/S2** (compare entries 11-13 with 2-4), suggesting that for such systems, there is no influence of the supporting order on catalyst activity.

#### **IV.2.2 Influence of $x_{Ni}$ and polymerization temperature on the polymer properties.**

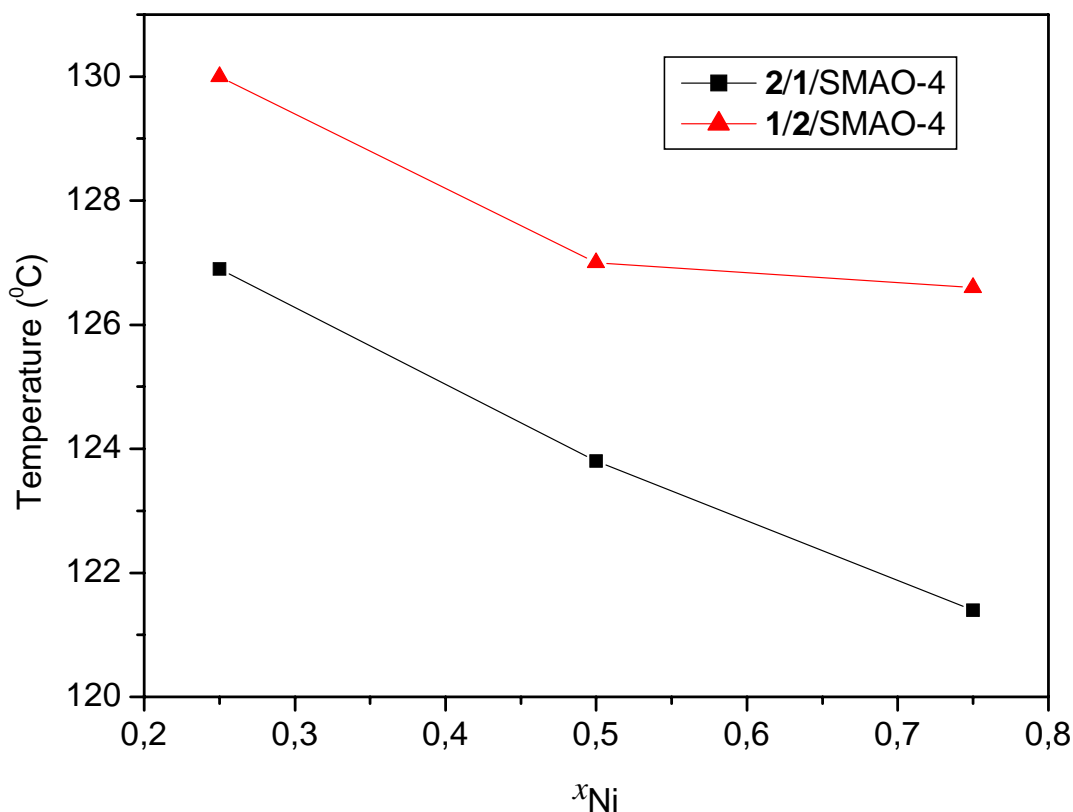
The influences of  $x_{Ni}$ , immobilization order and polymerization temperature on polyethylene microstructure have been evaluated by means of differential scanning calorimetry (DSC), and intrinsic viscosity. The results are summarized in Table IV.7. As expected, the branched polyethylene (BPE) produced by **1/S2** ( $x_{Ni} = 1.00$ ) has a  $T_m$  of 119°C while the linear polymer (LPE) produced by **2/S2** ( $x_{Ni} = 0.00$ ) has a  $T_m$  of 134°C. In contrast to the thermal behavior of the PE blends produced at 0°C using the homogeneous binary catalyst system  $Ni(\alpha\text{-diimine})Cl_2/rac\text{-etilenebis(IndH}_4)ZrCl_2$ ,<sup>120c</sup> single melting and crystallization peaks were observed in the blends produced by both **2/1/S2** and **1/2/S2** catalyst systems, indicating a good compatibility between the branched and linear PE phases (Figure IV.8). Furthermore,  $T_m$  is strongly influenced by the nickel molar fraction mainly for **2/1/S2** whereas the values varied from 121°C ( $x_{Ni} = 0.75$ ) to 127°C ( $x_{Ni} = 0.75$ ).

Surprisingly, the supporting order affects the melting temperature of the polymer blends as can be seen in Figure IV.9. The initial immobilization of **1** on the support (**2/1/S2**) leads to polymers with lower  $T_m$  than those obtained using **1/2/S2**. For instance, the  $T_m$  of the polymer produced by **2/1/S2** ( $x_{Ni} = 0.75$ ) is 121°C while that one obtained using **1/2/S2** is 127°C (compare entries 4 and 13). It can be speculated that the lower  $T_m$ 's found for polymers produced by **2/1/S2** can be associated to the presence of higher amount of Ni active species on the surface compared to **1/2/S2** which determine formation of higher quantity of BPE.



**Figure IV.8.** DSC thermograms of the polyethylenes produced by **2/1/S2** at 0°C.

At higher polymerization temperature (30°C), only a slightly decrease of  $T_m$  (from 138°C,  $x_{Ni} = 0.00$ ; to 134°C,  $x_{Ni} = 0.75$ ) with crystallinity varying from 28 to 40 % were observed. At this temperature, the polyethylenes formed by **1** are totally amorphous due to the higher branch content<sup>57b</sup> and apparently they do not interfere in the crystallization process of the linear polyethylenes.



**Figure IV.9.** Influence of the immobilization order and  $x_{Ni}$  on the melting temperature of the polyethylene blends produced at 0°C.

As expected, the polyethylenes produced by **2/S2** showed higher intrinsic viscosity  $[\eta]$  values (0°C, 7.47 dL/g; 30°C, 7.43 dL/g) than those obtained using **1/S2** (0°C, 4.81 dL/g; 30°C, 3.81 dL/g), since catalyst **2** produces higher molecular weight PE.<sup>97,125</sup> In contrast with the results obtained with homogeneous catalysts,<sup>120a,b</sup> the intrinsic viscosity values for the polymer produced using **2/1/S2** at 0 and 30°C do not show a direct correlation with  $x_{Ni}$ .

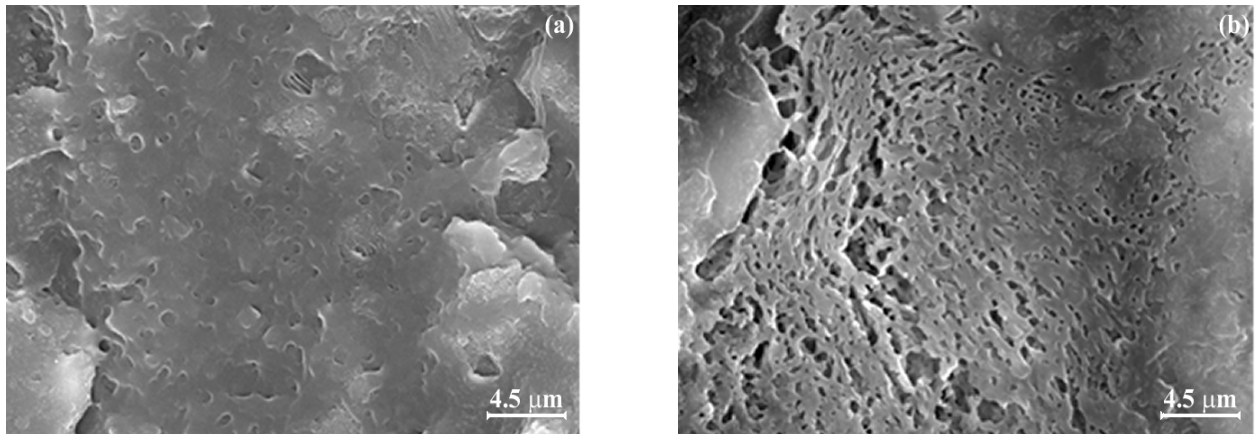
### IV.2.3 Morphology studies

The morphology of the polymer blends was investigated using scanning electron microscopy (SEM). SEM micrographs made on cryo-fractured surfaces of the polyethylene

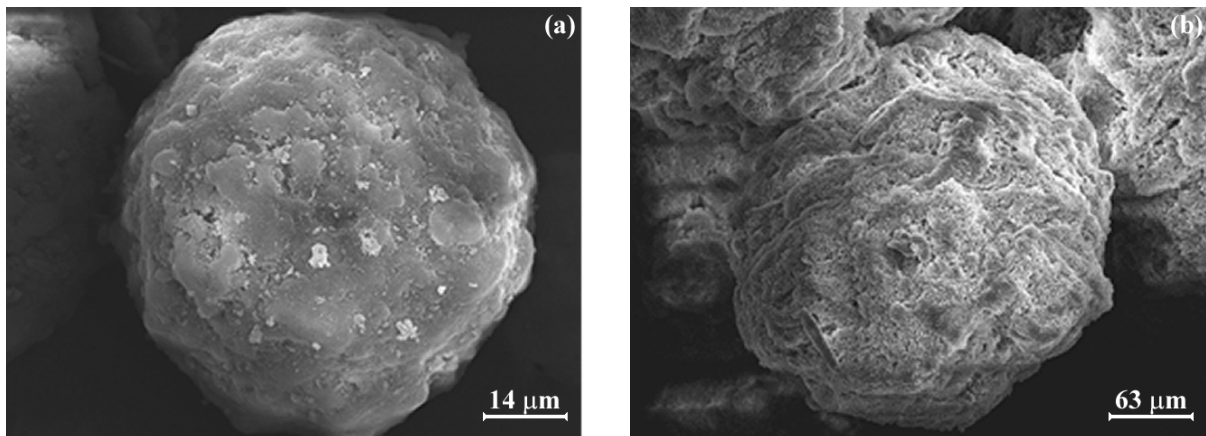
blend samples produced at 0°C are shown in Figure IV.10. In the SEM micrograph of the blend sample, it was not possible to distinguish the presence of two polymer phases (Figure IV.10a) indicating good dispersion between the polyethylene phases as consequence of the presence of low branch PE produced by nickel catalyst at this polymerization temperature. In order to evaluate the distribution of the PE phases in the matrix, the cryo-fractured surface was etched with hot *o*-xylene and studied by SEM. The Figure IV.10b shows the formation of holes distributed on LPE matrix as a consequence of the extraction of the branched PE produced by **1**.

SEM micrographs in the Figure IV.11 show the morphology of supported catalyst precursors, and the polyethylene produced by **2/1/S2** catalytic system. We observed that the spherical morphology of the *in situ* activated Ni and Ti catalyst precursors immobilized on MAO-modified silica is replicated in the polymer blend. The final size of polyethylene particles is about 287 μm (Figure IV.11b) in diameter, larger than the original support, which has a diameter around 70 μm (Figure II.1a).





**Figure IV.10.** SEM micrographs of BPE/HDPE blends crio-fractured surfaces produced by **2/1/S2** at 0 °C: (a)  $x_{Ni} = 0.50$ ; (b)  $x_{Ni} = 0.50$  after etched with o-xylene at 80 °C.



**Figure IV.11.** SEM micrographs: (a) **2/1/S2** ( $x_{Ni} = 0.50$ , 1500 x); (b) polyethylene blend produced by **2/1/S2** at 0°C ( $x_{Ni} = 0.50$ , 1500 x).

## V. CONCLUSIONS

---

The complex  $\text{Ni}(\alpha\text{-diimine})\text{Cl}_2$  (**1**) was impregnated and characterized on the supports **S1**, **S2**, **S3** and **S4**, which presented some activity in the ethylene polymerization. The amount of nickel in the support increases with the increase of the quantity of aluminum up to 8.0% wt of Al/SiO<sub>2</sub>, suggesting that **1** are associated, preferentially, to the MAO present in the surface. The activities of the supported catalysts, in the ethylene polymerization are influenced by the amount of aluminum in the support. **S1** showed be not active, in relation to **S2** and **S3**, the high catalytic activity was obtained using the supported system **1/S3** (196 kg of PE/mol[Ni].h.atm) indicate the formation of a stable catalytic species. The polymers produced by the supported catalysts showed are similar to the Ni homogenous. The best polymerization conditions, using the supported catalyst **S2**, was for hexane, MAO as cocatalyst, molar ratio Al/Ni of 1000 and temperature of 30°C (285 kg of PE/mol[Ni].h.atm). The DSC curves induced that the immobilization of **1** on the support provokes the formation of more crystalline than the Ni homogeneous.

Larger activities are obtained with the catalyst supported using the *in situ* methodology, under ethylene atmosphere, with which it was verified that the catalytic species formed starting from the reaction among the composed of nickel as composed alkylaluminium is not stable under atmosphere of argon. The catalyst supported in situ presents activity almost two times bigger than the systems prepared before the polymerization and the PEs produced showed similar properties, but with polydispersities around 2.0 suggesting that this process generates only one active specie on the support.

The *in situ* immobilization of precursor catalysts **1** and **2** on MAO-modified silica generates an effective heterogeneous catalyst for ethylene polymerization. Different types of polyethylene blends can be produced depending on the polymerization temperature, grafting order, and  $x_{\text{Ni}}$ . The absence of synergistic effect between the **1** and **2** species after immobilization on support can be associated to the presence of MAO that acts as spacer

keeping the Ti centers away from the Ni species. Catalyst activity was shown to be independent on the grafting order. On the other hand, this parameter has a strong influence on the melting temperature of the polymer blends. SEM micrograph showed that this heterogeneous catalytic system is able to produce PE blend with the improved morphology. The spherical shape of the PE particles corresponded to that of the silica support is in accordance with the known replication effect.

It was prepared and characterized a new complex of Cr<sup>III</sup> compounds having tridentated ligands (catalysts **3a-d**) which presented activity in the ethylene oligomerization. The crystal structure of **3c** confirms both the monomeric nature of the complex and  $\kappa^3$ -coordination of the ligand and the geometry around the chromium atom could be described as a distorted octahedron with the chlorine ligands in a *mer* disposition.

When compared to CrCl<sub>3</sub>(thf)<sub>3</sub>, with exception of **3a**, all chromium complexes showed active upon activation with (MAO) showing a differentiated effect in the TOF and not promote significant changes in the total C<sub>4</sub> and C<sub>6</sub> fractions. We found a production of lower amount of C<sub>8</sub> and higher amounts of C<sub>10</sub> and +C<sub>12</sub> oligomers fractions. The  $\alpha$ -olefins quantity increase when the ligands are uses. For the selectivity, was possible see a increase of  $\alpha$ -olefins quantity when the ligands are uses. The catalyst **3a** was not showed be active in the oligomerization reaction, but some activity in polymerization and the PE produced, at 3 and 20 atm of ethylene, showed by the DSC curves melting temperature peaks of 133.8 and 136 °C respectively indicating in both cases the production of high-density PE, and presented Mw of 46 647 g/mol with Mw/Mn = 2.4 (3 atm). The system **3c**/MAO was tested in different ethylene pressure (3 to 20 atm) showing slightly influence in the selectivity in dimmers, trimers, tetramers and pentamers. These results indicated that the use of higher ethylene pressure promotes higher selectivity.

## **VI. REFERENCES**

---

- 1 Theopold, K. H. *Chemtech* **1997**, 27, 26.
- 2 (a) Hogan, J. P.; Banks, R. L. U.S. Patent 2,825,721, 1958. (b) Hogan, J. P.; *J. Polym. Sci.* **1970**, 8, 2637. (c) McDaniel, M. P.; *Adv. Catal.* **1985**, 33, 47. (d) Clark, A.; *Catal. Rev.* **1970**, 3, 145. (e) Weckhuysen, B. M.; Wachs, I. E.; Shoonheydt, R. A.; *Chem. Rev.* **1996**, 96, 3327. (e) Weckhuysen, B. M.; Schoonheydt, R. A.; *Catal. Today* **1999**, 51, 215.
- 3 (a) Böhm, L. L.; *Angew. Chem. Int. Ed.* **2003**, 42, 5010. (b) Ziegler, K. Belgian Patent 533,362, 1954. (c) Ziegler, K.; Holzkamp, E.; Martin, H.; Breil, H.; *Angew. Chem.* **1955**, 67, 541. (d) Natta, G. J.; *Polym. Sci.* **1955**, 16, 143. (e) Natta, G.; *Angew. Chem. Int. Ed.* **1956**, 68, 393. (f) Wilke, G.; *Angew. Chem. Int. Ed.* **2003**, 42, 5000.
- 4 Brintzinger, H.H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem. Int. Ed.* **1995**, 34, 1143.
- 5 Duchateau, R.; *Chem. Rev.* **2002**, 102, 3525.
- 6 Gibson, V.C.; Spitzmesser, S.K.; *Chem. Rev.* **2003**, 103, 283.
- 7 Reto, M.A.S.; *Revista Plástico Moderno*. 2000, p.22.
- 8 Forte, M.C.; Miranda, M.S.L. & Duppont, J.; *Polímeros: Ciência e Tecnologia* 1996, p. 49.
- 9 Herfert, N., Fink, G.; *Makromol. Chem.* **1992**, 193, 1359.
- 10 (a) Wilke, G.; *Angew. Chem. Int. Ed. Engl.* **1988**, 27, 185. (b) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C.; *Angew. Chem. Int. Ed. Engl.* **1978**, 17, 466. (c) Klabunde, U.; Ittel, S. D.; *J. Mol. Catal.* **1987**, 41, 123. (d) Ostoja Starzewski, K. A.; Witte, J.; *Angew. Chem. Int. Ed. Engl.* **1985**, 24, 599. For recent reviews, see: (e) Ittel, S. D.; Johnson, L. K.; Brookhart, M.; *Chem. Rev.* **2000**, 100, 1169. (f) Ittel, S. D.; Johnson, L. K.; Brookhart, M.; *Chem. Rev.* **2000**, 100, 1169. (g) Mecking, S.; *Coord. Chem. Rev.* **2000**, 203, 325.
- 11 Johnson, L. K.; Killian, C. M.; Brookhart, M.; *J. Am. Chem. Soc.* **1995**, 117, 6414.

- 12 Schleis, T.; Spaniol T. P.; Okuda, J.; Heinemann J.; Mülhaupt, R. J.; *Organometal. Chem.* **1998**, *569*, 159.
- 13 Hlatky, G. G.; *Chem. Rev.* **2000**, *100*, 1347.
- 14 Janiak, B.C.; Rieger, B.; Voelkel, R.; Barun, H.G. . *J. of Polym. Sci.,A-Polym. Chem.* **1993**, *31*, 2959.
- 15 Gates, B. C.; *Catalytic Chemistry*. Singapura: John Wiley & Sons, **1992**.
- 16 Flemmert G. L. *Proc.-Fert. Soc.* **1977**, 163.
- 17 IUPAC, Manual of Symbols and Terminology, Appendix 2, Part I, Colloid and Surface Chemistry, *Pure Appl. Chem.* **1972**, *31*, 578.
- 18 Chien, J. C. W. *Top. Catal.* **1999**, *7*, 23.
- 19 Fink, G.; Steinmetz, B.; Zechlin, J.; Przybyla, C.; Tesche, B. *Chem. Rev.* **2000**, *100*, 1377.
- 20 (a) Ban, H.T.; Arai, T.; Ahn, C.-H.; Uozumi, T.; Soga, K.; *Curr. Trends Polym. Sci.* **1999**, *4*, 47. (b) Ribeiro, M.R.; Deffieux, A.; Portela, M.F.; *Ind. Eng. Chem. Res.* **1997**, *36*, 1224.
- 21 (a) dos Santos, J.H.Z.; Ban, H.T.; Teranishi, T.; Uozumi, T.; Sano, T.; Soga, K.; *J. Mol. Catal. A Chem.* **2000**, *158*, 541. (b) Tait, P.J.; Ediati, R. in: W. Kaminsky (Ed.), *Metalorganic Catalysts for Synthesis and Polymerization*, Springer, Heidelberg, 1999, p. 307.
- 22 Chen, E.Y.-X.; Marks, T.J.; *Chem. Rev.* **2000**, *100*, 1391.
- 23 Mason, M.R.; Smith, J.M.; Bott, S.G.; Barron, A.R.; *J. Am. Chem. Soc.* **1993**, *115*, 4971.
- 24 Barron, A.R. in: J. Scheirs, W. Kaminsky (Eds.), *Metallocene-based Polyolefins*, Wiley, West Sussex, 2000.
- 25 (a) Psynkiewicz, S.; *Polyhedron* **1990**, *9*, 429; (b) Sinn, H.; Bliemeister, J.; Clausnitzer, D.; Tikwe, L.; Winter, H.; Zarncke, O. in: W. Kaminsky, H. Sinn (Eds.), *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*, Springer, New York, 1988, p. 257; (c) Tritto, I.; Mealares, C.; Sacchi, M.C.; Locatelli, P.; *Macromol. Chem. Phys.* **1997**, *198*, 3963.

- 26 Eilertsen, J.L.; Rytter, E.; Ystenes, M.; *Vibrat. Spectrosc.* **2000**, *24*, 257.
- 27 Panchenko, V.N.; Zakharov, V.A.; Danilova, I.G.; Paukshtis, E.A.; Zakharov, I.I.; Goncharov, V.G.; Suknev, A.P.; *J. Mol. Catal. A: Chemical* **2001**, *174*, 107.
- 28 dos Santos, J. H. Z., Bianchini, D., Uozumi, T., Sano, T. *J. Mol. Catal. A: Chemical* **2002**, *3559*, 1.
- 29 Ogasawara, S.; *Shokubai* **1976**, *18*, 124.
- 30 dos Santos, J.H.Z.; Rosa, M.B.; Krug, C.; Stedile, F.C.; Haag, M.C.; Dupont, J.; Forte, M.C.; *J. Polym. Sci., Part A Polym. Chem.* **1999**, *37*, 1987.
- 31 (a) Zakharov, V.A.; Panchenko, V.N.; Semikolenova, N.V.; Danilova, I.G.; Paukshtis, E.A.; *Polym. Bull.* **1999**, *43*, 87. (b) Panchenko, V.N.; Semikolenova, N.V.; Danilova, I.G.; Paukshtis, E.A.; Zakharov, V.A.; *J. Mol. Catal. A: Chem.* **1999**, *142*, 27.
- 32 Muñoz-Escalona, A.; Méndez, L.; Sancho, J.; Lafuente, P.; Peña, B.; Michels, W.; Hidalgo, G.; Martínez-Nuñez, M.F.; in: Kaminsky, W. (Ed.), *Metalorganic Catalysts for Synthesis and Polymerization*, Springer, Heidelberg, 1999, p. 381.
- 33 Casagrande, A.C.A.; Tavares, T.T.R.; Kuhn, M.C.A.; Casagrande, O.L.; dos Santos, J.H.Z.; Teranishi T.; *J. Mol. Catal. A: Chem.* **2004**, *212*, 267.
- 34 Gil, M.P.; dos Santos, J.H.Z.; Casagrande, O.L.; *J. Mol. Catal. A: Chem.* **2004**, *209*, 163.
- 35 Johnson, L. K.; Killian, C. M. In *Metallocene-Based Polyolefins, Preparation, Properties and Technology*; Scheirs, J., Kaminsky, W., Eds.; Wiley: West Sussex, England, 2000; p 233.
- (b) Killian, C. M.; Brookhart, M.; Johnson, L. K.; Tempel, D.; Ittel, S. D.; McLain, S. J.; McCord, E. F. SPO 696, Proc. Int. Bus. Forum Spec. Polyolefins, 6th 1996, 117.
- 36 Ittel, S. D. In *Metalorganic Catalysts for Synthesis and Polymerization*; Kaminsky, W., Ed.; Springer-Verlag: Heidelberg, 1999; p 616. (b) Okuda, F.; *Idemitsu Giho* **1998**, *41 (1)*, 58.
- (c) Piccolini, R.; *J. ChemTech* **1999**, *29 (5)*, 39.



- 37 (a) Sugimura, K.; Ban, K.; Suzuki, Y.; Hayashi, T.; *Chem Abs.* **1998**, 128, 61920. (b) Sugimura, K.; Yorozu, K.; Suzuki, Y.; Hayashi, T.; *Chem Abs.* **1997**, 127, 359237.
- 38 Preishuber-Pfugl, P.; Brookhart, M. *Macromolecules* **2002**, 35, 6074.
- 39 Gates, D. P.; Svejda, S. K.; Onate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M.; *Macromolecules* **2000**, 33, 2320.
- 40 Chadwick, J. C.; Severn, J. R.; Castelli, V. van A.; *Macromolecules* **2004**, 37, 6258.
- 41 (a) Kunrath, F. A.; Mota, F. F.; Casagrande, O. L.; Mauler, R. S.; De Souza, R. F.; *Macromol. Chem. Phys.* **2002**, 203, 2407. (b) Simon, L. C.; Patel, H.; Soares, J. B. P.; De Souza, R. F.; *Macromol. Chem. Phys.* **2001**, 202, 3237. (c) AlObaidi, F.; Ye, Z.; Zhu, S.; *Macromol. Chem. Phys.* **2003**, 204, 1653. (d) Chien, J. C.W.; Fernandes, S.; Correia, S. G.; Rausch, M. D.; Dickson, L. C.; Marques, M. M.; *Polym. Int.* **2002**, 51, 729. (e) McLain, S. J.; McCord, E. F.; Johnson, L. K.; Ittel, S. D.; Nelson, L. T. J.; Arthur, S. D.; Halfhill, M. J.; Teasley, M. F.; Tempel, D. J.; Killian, C. M.; Brookhart, M.; *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, 38 (1), 772. (f) Jurkiewicz, A.; Eilerts, N. W.; Hsieh, E. T.; *Macromolecules* **1999**, 32, 5471.
- 42 (a) Bochmann, M.; *J. Chem. Soc. Dalton Trans.* **1996**, 255. (b) McKnight, A.L.; Waymouth, R.M.; *Chem Rev.* **1998**, 98, 2587.
- 43 (a) Stephan, D.W.; Guérin, F.; Spence, R.E.V.H.; Koch, L.; Gao, X.; Brown, S.J.; Swabey, J.W.; Wang, Q.; Xu, W.; Zoricak, P.; Harrison, D.G.; *Organometallics* **1999**, 18, 2046. (b) Lappert, M.F.; Deelman, B.J.; Hitchcock, P.B.; Leung, W.P.; Lee, H.K.; Mak, T.C.W.; *Organometallics* **1998**, 18, 1444, and references reported therein.
- 44 (a) Ziegler, K.; *Angew. Chem.* **1964**, 76, 545. (b) Natta, G.; *Angew. Chem.* **1964**, 76, 553.
- 45 Karbasheski, E.; Kale, L.; Rudin, A.; Tchir, W. J.; *J. Appl. Polym. Sci.* **1993**, 47, 1143.
- 46 Utracki, L. A.; Schlund, B. *Polym. Eng. Sci.* **1987**, 27, 1512.

47 Manson, J.A.; Sperling, L.H.; *Polymer Blends and Composites*, Plenum Press, New York 1976.

48 (a) Scheirs, J.; Böhm, L.L.; Boot, J.C.; Leever, P.S.; *Trends Polym. Sci.* **1996**, *4*, 408. (b) Böhm, L.L.; Enderle, H.F.; Fleissner, M. in: *Catalyst Design for Taylor-Made Polyolefins*, K. Soga, M. Terano, (Eds.), Elsevier: Amsterdam 1994, p. 351; (c) Soares, J.B.P.; Hamielec, A.E.; *Polym. React. Eng.* **1996**, *4*, 153.

49 Ahn, T.O.; Hong, S.C.; Kim, J.H.; Lee, D.; *J. Appl. Polym. Sci.* **1998**, *67*, 2213.

50 (a) Lee, D.; Yoon, K.; Noh, S.; Kim, S.; Huh, W.; *Macromol. Rapid Commun.*, **1996**, *17*, 639. (b) Barnhart, R.; Bazan, G.C.; *J. Am. Chem. Soc.*, **1998**, *120*, 1082. (c) Yan, X.; Chernega, A.; Grenn, M.L.H.; Sanders, J.; Souter, J.; Ushioda, D.; *J. Mol. Catal. A*, **1998**, *128*, 119. (d) Mecking, S.; *Macromol. Rapid Commun.*, **1999**, *20*, 139.

51 (a) US 6,207,606 (2001), Univation Technologies, LLC, invs.: C.-T. Lue, D. J. Crowther; Chem Abstr. 2001, 132, 003599 g; (b) EP 893455 (2000), Mitsui Chemicals, invs.: K. Sugimura, K. Yorozu, Y. Suzuki, T. Hayashi, S. Matsunaga; Chem. Abstr. 1997, 127, 319388a; (c) WO 50475 (2000), Eastman Chemical Company, invs.: C. Killian, P. Mackenzie, J. Ponasik, L. Moody; Chem. Abstr. 2000, 133, 193627f; (d) EP 1005473 (2000), Borealis, invs.: O. Andell, J. Maaranen; Chem. Abstr. 1999, 130, 210102p; (e) WO 57159 (1999), Exxon Chemical Patents Inc., inv.: P. Matsunaga; Chem. Abstr. 1999, 131, 351802z; (f) WO 10391 (1999), Du Pont, invs.: E. B. Coughlin, S. D. Arthur, S. D. Ittel; Chem. Abstr. 1999, 130, 197106w; (g) WO 50318 (1999), Du Pont, invs.: A. M. A. Bennett, J. D. Citron, E. B. Coughlin, L. Wang; Chem. Abstr. 1999, 131, 272334v; (h) JP 10330415 (1998), Mitsui Chemicals, invs.: K. Sugimura, J. Saito, T. Fujita; Chem. Abstr. 1999, 130, 082005v; (i) JP 10231395 (1998), Sumitomo Chemical, invs.: O. Yoshiaki, E. Naofumi, O. Nobuo; Chem. Abstr. 1998, 129, 203745b; (j) WO 38228 (1998), Targor, inv.: S. Mecking; Chem. Abstr. 1998, 129, 189790d; k WO 48735 (1997), Exxon Chemical, invs.: J. A. M. Canich, G. A.

Vaughan, P. T. Matsunaga, D. E. Gindelberger, T. D. Shaffer, K. R. Squire; Chem. Abstr. 1998, 128, 89234m; (l) EP 503791 (1997), Mobil Oil Corporation, invs.: A. H. Ali, R. O. Hagerty, S. C. Ong; Chem. Abstr. 1993, 118, 039620 g; (m) US 5,534,473 (1996), Phillips Petroleum Company, invs.: M. B. Welch, R. L. Geerts, S. J. Palackal, T. M. Pettijohn; Chem. Abstr. 1996, 125, 34360 g; (n) US 5,350,817 (1994), Hoechst AG, invs.: A. Winters, V. Dolle, W. Spaleck; Chem. Abstr. 1993, 119, 96396 h; (o) U.S. 5,331,070 (1994), Phillips Petroleum Co., invs.: T. M. Pettijohn, W. K. Reagen, S. J. Martin; Chem. Abstr. 1995, 122, 056808z; (p) EP 128045 (1991), Exxon Research & Engineering Company, invs.: J. A. Ewen, H. C. Welborn; Chem. Abstr. 1985, 102,185662 h; (q) US 4,937,299 (1990), Exxon Research & Engineering Company, invs.: J. A. Ewen, H. C. Welborn; Chem. Abstr. 1985, 102, 149941q; (r) US 4,975,403 (1990), Fina Technology, Inc., inv.: J. A. Ewen; Chem. Abstr. 1989, 111, 154553e; (s) U.S. 4620021 (1986), Bayer A.-G., invs.: K. H. A Ostoja Starzewski, J. Witte, H. Bartl; Chem. Abstr. 1985, 103, 142517t.

52 (a) WO48735 (1997), Exxon Chemical, invs.: J. A. M. Canich, G. A. Vaughan, P. T. Matsunaga, D. E. Gindelberger, T. D. Shaffer, K. R. Squire; Chem Abs. 1998, 128, 89234m. (b) Yan, X.; Chernega, A.; Grenn, M.L.H.; Sanders, J.; Souter, J.; Ushioda, T.; *J. Mol. Catal. A* **1998**, *128*, 119.

53 Chu, K.J.; Soares, J.B.P.; Penlidis, A.; *Macromol. Chem. Phys.* **2000**, *201*, 340. (b) Chu, K.J.; Soares, J.B.P.; Penlidis, A.; *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 462.

54 Franceschini, F.C.; Tavares, T.T.R.; Greco, P.P.; Bianchini, D.; Stedile, F.C.; Galland, G.B.; dos Santos, J.H.Z.; Soares, J.B.P.; *Journal of Molecular Catalysis A: Chemical*, **2003** *202*, 127.

55 Park, Y.H.; Lee, H.W.; Ahn, S.H.; *Journal of Molecular Catalysis A: Chemical*, **2003**, *194*, 19.

- 56 Soares, J.B.P.; de Souza, R.F.; Simon, L.C.; Patel, H.; *Macromol. Chem. Phys.* **2001**, *202*, 3237.
- 57 Simon, L.C.; Mauler, R.S.; de Souza, R.F.; *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 4656.
- 58 (a) Parshall, G.W., Ittel, S.D., Homogeneous Catalysis, Wiley & Sons Inc., New York: USA, 1992. (b) Rieger, B., Chien, J.C.W., *Polym. Bull.* **1989**, *21*, 159.
- 59 (a) Tait, P.J.T., Berry, I.G., Comprehensive Polymer Science, Vol. 4 (Eds. Eastmond, G.C., Ledwith, A., Russo, S., Sigwalt, P.), Pergamon Press, Oxford, 1989, p. 575 (b) Encyclopedia of Polymer Science and Engineering, Vol. 6 (Eds. Mark, H.F., Bikales, N.B., Overberger, C.G., Menges, G., Kroschwitz, J.I.), John Wiley & Sons, New York, 1986, p. 429.
- 60 Alpha Olefins (02/03-4), PERP Report, Nexant Chem Systems.
- 61 Skupinska, J.; *Chemical Reviews* **1991**, *91*, 613.
- 62 Linear Alpha Olefins, CEH Marketing Research Report, September 2000.
- 63 M. Zahoor, F. Al-Sherehy, O. Alabisi, M.M. Abdillahi, M.R. Saeed, US 6184428 (Saudi Basic Industries Corporation), February 6, 2001.
- 64 R.M. Manyik, W.E. Walker, T.P. Wilson, US 3300458 (Union Carbide Corporation), January 24, 1967.
- 65 Manyik, R.M.; Walker, W.E.; Wilson, T.P.; *J. Catal.* **1977**, *47*, 197.
- 66 W.K. Reagan, Symp. Prepr. Conv. Light Olefins, Div. Pet. Chem., Am. Chem. Soc. 34 (1989) 583.
- 67 Theopold, K.H.; *Eur. J. Inorg. Chem.* **1998**, 15.
- 68 (a) Emrich, R.; Heinemann, O.; Jolly, P.W.; Krüger, C.; Verhovnik, G.P.J.; *Organometallics* **1997**, *16*, 1511. (b) Jolly, P.W.; *Acc. Chem. Res.* **1996**, *29*, 544.

- 69 (a) Mahomed, H.; Bollmann, A.; Dixon, J.; Gokul, V.; Griesel, L.; Grove, C.; Hess, F.; Maumela, H.; Pepler, L.; *Appl. Catal. A* **2003**, 255, 355. (b) J.J.C. Grove, H.A. Mahomed, L. Griesel, WO 03/004158 (Sasol Technology (Pty Ltd), June 27, 2002.
- 70 J.R. Briggs, US 4668838 (Union Carbide Corporation), May 26, 1987.
- 71 Briggs, J.R.; *Chem. Commun.* **1989**, 11, 674.
- 72 I.J. Levine, F.J. Karol, US 4777315 (Union Carbide Corporation), October 11, 1988.
- 73 H. Sato, S. Suzuki, JP 07215896 (Idemitsu Chemical Company), August 15, 1995.
- 74 F.J. Wu, EP 0537609 (Albemarle Corporation), July 10, 1992.
- 75 (a) J.W. Freeman, J.L. Buster, R.D. Knudsen, US 5,856,257 (Phillips Petroleum Company), January 5, 1999. (b) W.K. Reagan, J.W. Freeman, B.K. Conroy, T.M. Pettijohn, E.A. Benham, US 5,451,645 (Phillips Petroleum Company), September 19, 1995. (c) E. Tanaka, H. Urata, T. Oshiki, T. Aoshima, R. Kawashima, S. Iwade, H. Nakamura, S. Katsuki, T. Okanu, EP 0 611 743 (Mitsubishi Chemical Corporation), August 24, 1994. (d) Y. Araki, H. Nakamura, Y. Nanba, T. Okanu, US 5,856,612 (Mitsubishi Chemical Corporation), January 5, 1999.
- 76 Reger, D.L.; *Comments Inorg. Chem.* **1999**, 21, 1.
- 77 T. Yoshida, T. Yamamoto, H. Okada, H. Murakita, US2002/0035029 (Tosoh Corporation), March. 21, 2002.
- 78 F.J. Wu, US 5811618 (Amoco Corporation), August 25, 1995.
- 79 S.J. Dossett, A. Gillon, A.G. Orpen, J.S. Fleming, P.G. Pringle, D.F. Wass, M.D. Jones, *Chem. Commun.* (2001) 699.
- 80 Cooley, N.A.; Green, S.M.; Wass, D.F.; Heslop, K.; Orpen, A.G.; Pringle, P.G.; *Organometallics* **2001**, 20, 4769.
- 81 D.F. Wass, WO 02/04119 (BP Chemicals Ltd), January 17, 2002.

- 82 Carter, A.; Cohen, S.A.; Cooley, N.A.; Murphy, A.; Scutt, J.; Wass, D.F.; *Chem. Commun.* **2002**, 858.
- 83 J.T. Dixon, J.J.C. Grove, P. Wasserscheid, D.S. McGuinness, F.M. Hess, H. Maumela, D.H. Morgan, A. Bollmann, WO 03053891 (Sasol Technology (Pty) Ltd), December 20, 2001.
- 84 McGuinness, D.S.; Wasserscheid, P.; Keim, W.; Dixon, J.T.; Grove, J.J.C.; Hu, C.; Englert, U.; *Chem. Commun.* **2003**, 334.
- 85 (a) McGuinness, D.S.; Wasserscheid, P.; Keim, W.; Morgan, D.H.; Dixon, J.T.; Bollmann, A.; Maumela, H.; Hess, F.M.; Englert, U.; *J. Am. Chem. Soc.* **2003**, *125*, 5272. (b) J.T. Dixon, P. Wasserscheid, D.S. McGuinness, F.M. Hess, H. Maumela, D.H. Morgan, A. Bollmann, WO 03053890 (Sasol Technology (Pty) Ltd), December 20, 2001.
- 86 M. Bluhm, O. Walter, M. Döring, Poster 126 at the XXXVII Jahrestreffen Deutscher Katalytiker, 17–19 March 2004 held in Weimar, Germany.
- 87 (a) Schulz, G.V.Z.; *Phys. Chem. Abt. B* **1935**, *30*, 379. (b) Schulz, G.V.Z.; *Phys. Chem. Abt. B* **1939**, *43*, 25. (c) Flory, P.J.; *J. Am. Chem. Soc.* **1940**, *62*, 1561.
- 88 (a) Cossee, P.; *J. Catal.* **1964**, *3*, 80. (b) Arlman, E.J.; Cossee, P.; *J. Catal.* **1964**, *3*, 99.
- 89 (a) McDermott, J.X.; White, J.F.; Whitesides, G.M.; *J. Am. Chem. Soc.* **1973**, *95*, 4451. (b) McDermott, J.X.; White, J.F.; Whitesides, G.M.; *J. Am. Chem. Soc.* **1976**, *98*, 6521.
- 90 McDaniel, M.P.; *Adv. Catal.* **1985**, *33*, 47.
- 91 Meijboom, N.; Schaverien, C.J.; Orpen, A.G.; *Organometallics* **1990**, *9*, 774.
- 92 Köhn, R.D.; Haufe, M.; Mihan, S.; Lilge, D.; *Chem. Commun.* **2000**, 1927.
- 93 (a) Morgan, D.H.; Schwikkard, S.L.; Dixon, J.T.; Nair, J.J.; Hunter, R.; *Adv. Synth. Catal.* **2003**, *345*, 939. (b) van Rensburg, W.J.; Grove, C.; Steynberg, J.P.; Stark, K.B.; Huyser, J.J.; Steynberg, P.J.; *Organometallics* **2004**, *23*, 1207.

- 94 Wang, Y.; Ohishi, Y.; Shishido, T.; Zhang, Q. H.; Yang, W.; Guo, Q.; Wan, H. L.; Takehira, K.; *J. Catal.* **2003**, *220*, 347.
- 95 (a) Espelid, O.; Borve, K. J.; *J. Catal.* **2000**, *195*, 125. (b) Espelid, O.; Borve, K. J.; *J. Catal.* **2002**, *206*, 331.
- 96 van Koten, G.; Vrieze, K.; Stone A.; West, R.; *Adv. Organomet. Chem*; **1982**, *21*, 169.
- 97 Murtuza, S.; Casagrande, O. L.; Jordan, R.F.; *Organometallics* **2002**, *21*, 1882.
- 98 Bianchini, D.; dos Santos, J.H.Z.; Uozumi, T.; Sano, T.; *J. Mol. Catal. A: Chemical* **2000**, *185*, 223.
- 99 Sorrell, T. N.; Malachowski, M. R.; *Inorg. Chem.* **1983**, *22*, 1883.
- 100 Martens, C. F.; Schenning, A. P. H. J.; Feiters, M. C.; Berens, H. W.; van der Linden, J. G. M, Admiraal G.; Beurskens, P. T.; Kooijman, H.; Spek, A. L.; Noltela R. J. M.; *Inorg. Chem.* **1995**, *34*, 4735.
- 101 Chee, K.K.; *J. Appl. Polim. Sci.* **1985**, *30*, 1359.
- 102 Johnson, L. K.; Killian, C. M.; Arthur, S. D.; Feldman, J.; McCord, E. F.; McLain, S. D.; Kreutzer, K. A.; Bennett, A. M.; Coughlin, E. B.; Ittel, S. D.; Parthasarathy, A.; Tempel, D. J.; Brookhart, M. S. WO 9623010.
- 103 Ciesla, U.; Schuth, F.; *Microporous and Mesoporous Materials* **1999**, *27*, 131.
- 104 R. K. Iler. *The Chemistry of Silica*. John Wiley & Sons, New York 1979.
- 105 Haag, M. C.; Dupont, J.; Stedile, F.C.; dos Santos, J.H.Z.; *J. Mol. Catal. A: Chemical* **2002**, *197*, 223.
- 106 Bianchini, D.; Bichinho, K. M.; dos Santos, J.H.Z.; *Polymer.* **2002**, *43*, 2937.
- 107 A. Muñoz-Escalona, L.Méndez, J. Sancho, P. Lafuente, B. Peña, W. Michiels, G. Hidalgo, M. F. Martínez-Niñes In: W. Kaminsky (Ed.), *Metalorganic Catalysts for Synthesis and Polymerization*, Springer, 1999, p.381.

- 108 (a) McConville, D. H.; Scollard, J. D.; *J. Am. Chem. Soc.* **1996**, *118*, 10008. (b) McConville, D. H.; Scollard, J. D.; Vittal, J. J.; Payne, N. C.; *J. Mol. Catal. A: Chemical* **1998**, *128*, 201.
- 109 Mota, F.F.; Mauler, R.S.; de Souza, R.F.; Casagrande, O.L.; *Polymer* **2003**, *44*, 4127.
- 110 Peruch, F.; Cramail, H.; Deffieux, A.; *Macromolecules* **1999**, *32*, 7977.
- 111 Casagrande, A.C.A.; Tavares, T.T.R.; Kuhn, M.C.A.; Casagrande Jr, O.L. dos Santos, J.H.Z.; Teranishi, T.; *Journal of Molecular Catalysis A: Chemical* **2004**, *212*, 267.
- 112 Alt, H.G.; Koppl, A.; *Chem. Rev.* **2000**, *100*, 1205.
- 113 (a) Schuman, T.; Stepanov, E.V.; Nazarenko, S.; Capaccio, G.; Hiltner, A.; Baer, E.; *Macromolecules* **1998**, *31*, 4551; (b) Wignall, G.D.; Alamo, R.G.; Londono, J.D.; Mandelkern, L.; Kim, M.H.; Lin, J.S.; Brown, G.M.; *Macromolecules* **2000**, *33*, 551; (c) Agamalian, M.; Wignall, G.D.; Alamo, R.G.; Londono, J.D.; Kim, M.H.; Mandelkern, L.; *Macromolecules* **1999**, *32*, 3093.
- 114 (a) Komon, Z.J.A.; Bazan, G.C.; *Macromol. Rapid Commun.* **2001**, *22*, 467; (b) de Souza, R.F.; Casagrande, O.L.; *Macromol. Rapid Commun.* **2001**, *22*, 1293. (c) Sperber, O.; Kaminsky, W.; *Macromolecules* **2003**, *36*, 9014. (d) Soares, J.B.P.; Kim, J.D.; *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 1408; (e) Soares, J.B.P.; Kim, J.D.; *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 1417; (f) Soares, J.B.P.; Beigzadeh, D.; Duever, T.A.; da Silva Filho, A.A.; *Polym. React. Eng.* **2000**, *8*, 241; (g) Markel, E.J.; Weng, W.; Peacock, A.J.; Dekmenziann, A.H.; *Macromolecules* **2000**, *33*, 8541.
- 115 (a) Komon, Z.J.A.; Bu, X.; Bazan, G.C.; *J. Am. Chem. Soc.* **2000**, *122*, 1830; (b) Abramo, G.P.; Li, L.; Marks, T.J.; *J. Am. Chem. Soc.* **2002**, *124*, 13966.
- 116 (a) Komon, Z.J.A.; Diamond, G.M.; Leclerc, M.K.; Murphy, V.; Okazaki, M.; Bazan, G.C.; *J. Am. Chem. Soc.* **2002**, *124*, 15280; (b) Quijada, R.; Rojas, R.; Bazan, G.; Komon, Z.J.A.; Mauler, R.S.; Galland, G.B.; *Macromolecules* **2001**, *34*, 2411.



117 (a) Read, D.J.; Soares, J.B.P.; *Macromolecules* **2003**, *36*, 10037. (b) Iedema, P.D.; Hoefsloot, H.C.J.; *Macromolecules* **2003**, *36*, 6632. (c) Beigzadeh, D.; Soares, J.B.P.; Duever, T.A.; *Macromol. Rapid Commun.* **1999**, *20*, 541. (d) Beigzadeh, D.; Soares, J.B.P.; Hamielec, A.E.; *J. Appl. Polym. Sci.* **1999**, *71*, 1753. (e) Beigzadeh, D.; Soares, J.B.P.; Hamielec, A.E.; *Polym. React. Eng.* **1997**, *5*, 143; (f) Soares, J.B.P.; *Macromol. Theory Simul.* **2002**, *11*, 184.

118 Bruaseth, I.; Rytter, E.; *Macromolecules* **2003**, *36*, 3026.

119 (a) Rodrigues, S.; Silveira, F.; dos Santos, J.H.Z.; Ferreira, M.L.; *J. Mol. Catal. A: Chem.* **2004**, *216*, 19. (b) Silveira, F.; Loureiro, S.R.; de Galland, G.B.; Stedile, F.C.; dos Santos, J.H.Z.; Teranishi, T.; *J. Mol. Catal. A: Chem.* **2003**, *206*, 389. (c) dos Santos, J.H.Z.; Gerbase, A.E.; Rodenbusch, K.C.; Pires, G.P.; Martinelli, M.; Bichinho, K.M.; *J. Mol. Catal. A: Chem.* **2002**, *184*, 167. (d) Kim, J.D.; Soares, J.B.P.; *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 1427. (e) Kim, J.D.; Soares, J.B.P.; Rempel, G.L.; *Macromol. Rapid Commun.* **1998**, *19*, 197.

120 (a) Kunrath, F.A.; de Souza, R.F.; Casagrande, O.L.; *Macromol. Rapid. Commun.* **2000**, *121*, 277. (b) Kunrath, F.A.; Mauler, R.S.; de Souza, R.F.; Casagrande, O.L.; *Macromol. Chem Phys.* **2002**, *203*, 2058. (c) Mota, F.F.; de Souza, R.F.; Mauler, R.S.; Casagrande, O.L.; *Macromol. Chem Phys.* **2001**, *202*, 1016. (d) Mota, F.F.; de Souza, R.F.; Mauler, R.S.; Casagrande, O.L.; *Polymer* **2003**, *44*, 4127.

121 Kunrath, F.A.; Furlan, L.G.; de Souza, R.F.; Casagrande, O.L.; *J. Mol. Catal: Chemical* **2004**, *214*, 207.

122 Junges, F.; dos Santos, J.H.Z.; Casagrande, O.L. (manuscript in preparation).

123  $x_{Ni}$  is defined as the nickel mole fraction calculated from  $[Ni]/([Ni] + [Ti])$ .

124 Predicted activity= [activity of catalyst 1 x mole fraction of catalyst 1] + [activity of catalyst 2 x mole fraction of catalyst 2].

125 Gil, M.P.; dos Santos, J.H.Z.; Casagrande, O.L.; *Macromol. Chem and Phys.* **2001**, *202*, 319.

126 Keim, W.; Kowaldt, F.H.; Goddard, R.; Krüger, C.; *Angew. Chem.* **1978**, *90*, 493.

127 K. Weissermel, H.-J. Arpe, *Industrial Organic Chemistry*, Wiley-VCH Publishers, 1998.

128 McGuinness, D.S.; Gibson, V.C.; Wass, D.F.; Steed, J. W.; *J. Am. Chem. Soc.* **2003**, *125*, 12716.

# Livros Grátis

( <http://www.livrosgratis.com.br> )

Milhares de Livros para Download:

[Baixar livros de Administração](#)

[Baixar livros de Agronomia](#)

[Baixar livros de Arquitetura](#)

[Baixar livros de Artes](#)

[Baixar livros de Astronomia](#)

[Baixar livros de Biologia Geral](#)

[Baixar livros de Ciência da Computação](#)

[Baixar livros de Ciência da Informação](#)

[Baixar livros de Ciência Política](#)

[Baixar livros de Ciências da Saúde](#)

[Baixar livros de Comunicação](#)

[Baixar livros do Conselho Nacional de Educação - CNE](#)

[Baixar livros de Defesa civil](#)

[Baixar livros de Direito](#)

[Baixar livros de Direitos humanos](#)

[Baixar livros de Economia](#)

[Baixar livros de Economia Doméstica](#)

[Baixar livros de Educação](#)

[Baixar livros de Educação - Trânsito](#)

[Baixar livros de Educação Física](#)

[Baixar livros de Engenharia Aeroespacial](#)

[Baixar livros de Farmácia](#)

[Baixar livros de Filosofia](#)

[Baixar livros de Física](#)

[Baixar livros de Geociências](#)

[Baixar livros de Geografia](#)

[Baixar livros de História](#)

[Baixar livros de Línguas](#)

[Baixar livros de Literatura](#)  
[Baixar livros de Literatura de Cordel](#)  
[Baixar livros de Literatura Infantil](#)  
[Baixar livros de Matemática](#)  
[Baixar livros de Medicina](#)  
[Baixar livros de Medicina Veterinária](#)  
[Baixar livros de Meio Ambiente](#)  
[Baixar livros de Meteorologia](#)  
[Baixar Monografias e TCC](#)  
[Baixar livros Multidisciplinar](#)  
[Baixar livros de Música](#)  
[Baixar livros de Psicologia](#)  
[Baixar livros de Química](#)  
[Baixar livros de Saúde Coletiva](#)  
[Baixar livros de Serviço Social](#)  
[Baixar livros de Sociologia](#)  
[Baixar livros de Teologia](#)  
[Baixar livros de Trabalho](#)  
[Baixar livros de Turismo](#)