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Research Highlights

- Three β -diimine ligands and their corresponding nickel-complexes were synthesized;
- Hybrid silica containing β -diimine groups were prepared by sol-gel process;
- Hybrid silica were complexed with nickel to form heterogenized nickel-complex;
- Ethylene oligomerisation using nickel-β-diimines were described;
- Ligands nature were correlated with the catalytic activity and selectivity.

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Ethylene oligomerization using nickel-β-diimine hybrid xerogels produced by the sol-gel process

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Abstract

Nickel- β -diimine complexes have been used as homogeneous- and heterogeneousphase oligomerization catalysts. The following complexes have also been heterogenized on silica using the sol-gel method: 1,5-*bis*(phenyl)-pentanediimine-dibromonickel(II) (**A**), 1,5*bis*(2,6-dimethylphenyl)-2,4-pentanediimine-dibromonickel(II) (**B**) and 1,5-*bis*(2,4,6trimethylphenyl)-2,4-pentanediimine-dibromonickel(II) (**C**). The synthesis of the xerogels was performed employing 3-chloropropyltrimethoxysilane (CPTMS), tetraethylorthosilicate (TEOS) and HF. The hybrid β -diimine/silica materials are used in combination with ethylaluminum sesquichloride (EASC) and have been shown to be outstanding ethylene oligomerization catalyst systems. Under mild reactions conditions, the homogeneous and heterogenized catalysts had high turnover frequencies (between 1800 and 210000 h⁻¹). The best selectivities were obtained with the heterogenized catalysts, which give 100 % of C₄ fraction with 1-butene selectivities of up to 91 %.

Keywords: Oligomerization, Ethylene, β -Diimine, Xerogel, Sol-gel process, Organic-inorganic hybrid materials.

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Graphical Abstract

Hybrid silica was synthesized by the sol-gel method and subsequently complexed with metal to form a heterogenized nickel- β -diimine/silica complex, which was employed in ethylene-oligomerization reactions.

INSERT FIGURE ABSTRACT

1. Introduction

The oligomerization of olefins is an attractive method for producing longer chain olefins. Olefin oligomers are used in several applications, ranging from fuel components for better performance gasolines to intermediates for the manufacture of petrochemicals, such as plasticizers and lubricants [1-5]. Most of the olefin-oligomerization processes use transition metal catalysts, and a large variety of ligands containing O, N and P heteroatoms have been described. The proper choice of transition metal, organic ligands and co-catalysts enable some degree of tunability of the selectivity, ensuring production of the desired olefins.

Much effort has been devoted to studying the effects of the ligand structure of transition metal complexes on their catalytic properties in oligo/polymerization reactions [6-9]. β -Diimine and β -diiminate ligands are easy to prepare and have several attractive properties, including tunable electronic and steric parameters, which affect the catalytic performance of their transition metal complexes [10,11]. The β -diimine ligands have become more popular since the discovery by Feldman and co-workers of their use with nickel and palladium catalysts [12,13]. The first palladium β -diimine complex was obtained from the reaction of β -iminoamine with [Pd(CH₃CN)₄][BF₄]₂. β -Diimine ligands containing bulky aryl substituents on nitrogen atoms have been used in transition metals complexes with nickel for the successful synthesis of polyolefins [14,15].

Homogeneous catalysts usually contain uniform and well-defined active sites, which lead to high activities and reproducible selectivities. However, the major drawback in using these catalysts is the difficulty in separating the catalysts, products and solvent. An alternative to circumvent this drawback is to immobilize the homogeneous catalyst in various media, including inorganic and organic supports [16-19].

Sol-gel chemistry can play a central role in the development of hybrid materials because of the mild synthesis conditions provided by these processes [20]. The sol-gel process has received much attention in materials research due to its unique advantages such as low processing temperatures, high homogeneity of the final product and capacity to generate materials with surface-controlled properties. Materials with these properties are suitable for use as catalyst supports. The possibility of combining properties of organic and inorganic components in a unique composite material is a distinct characteristic of these materials because their properties are related not only to the chemical nature of the inorganic and organic components but also to their synergy. Therefore, the interface between inorganic and organic constituents strongly influences their properties. Organic-inorganic hybrid materials thus represent a creative alternative to design new materials and compounds and allow for the development of materials for innovative applications [21]. In this context, one attractive use is the immobilization of transition metal complexes in inorganic networks by sol-gel processes, producing heterogeneous hybrid-catalyst precursors. The production of ethylene oligomers using these heterogeneous catalytic systems provides a compelling answer to the demand for environmentally friendly processes by allowing for the recycling of the catalyst in contrast to the homogeneous-phase methods.

Despite the considerable interest in the application of hybrid systems as catalysts, surprisingly few studies have been devoted to describing their behavior. Important examples are the reports on the use of Fe, Re, Ti and Mo hybrid materials produced via sol-gel methods in epoxidation reactions [22-26] and Zr hybrid materials in ethylene polymerization [27-29]. Ethylene polymerization with nickel- β -diimine complexes immobilized in sol-gel hybrid materials was described in 2008 [30]; however, to the best of our knowledge, there are no examples of organic-inorganic hybrid materials prepared by the sol-gel method used for ethylene oligomerization available in the current literature.

We describe herein the synthesis of nickel- β -diimine complexes, their heterogenization in a hybrid silica-based matrix using the sol-gel process and their catalytic activities in ethylene oligomerization.

2. Experimental

All experiments were performed under an argon atmosphere using standard Schlenk-tube techniques. The solvents were deoxygenated by refluxing over appropriate drying agents (toluene, hexane, ethyl ether and benzene on sodium benzophenone and dichloromethane and acetonitrile on phosphorous pentoxide) under argon and distilled immediately prior to use. Methanol, ethanol and tetrahydrofuran (THF) were used without further purification. Aniline, 2,6-dimethylaniline and 2,4,6-trimethylaniline were purchased from Aldrich and distilled under reduced use. 3pressure prior to Chloropropyltrimethoxysilane (CPTMS), tetraethylorthosilicate (TEOS), sodium hydride (NaH) and anhydrous nickel bromide (NiBr₂) were purchased from Aldrich. p-Toluenesulfonic acid (Vetec) was distilled on benzene by the Dean-Stark technique. Sodium carbonate was purchased from Vetec and used without further purification. Ethylaluminum sesquichloride (Al₂Et₃Cl₃, EASC) was supplied by Akzo Nobel and used with previous dilution with toluene. Solids were dried under reduced pressure.

Elemental analyses were carried out in a Perkin Elmer M CHN Analyzer 2400. Infrared analyses were performed in an FT-IR Shimadzu Prestige-21 instrument using selfsupported pellets (without the use of KBr) of 40-50 mg of the sample. The results were obtained from the accumulation of 32 scans. The ¹H NMR spectra of the samples dissolved in CDCl₃ were obtained in an Inova 300 MHz spectrometer. UV-Vis absorption of the samples was measured in a spectral range from 200 nm to 800 nm using a Varian Carry 100 spectrophotometer equipped with a photomultiplier detector and diffuse reflectance accessory. Thermogravimetric analyses were performed on a TA Instruments TGA Q50. The samples were heated at 10 °C/min from 20 °C to 800 °C under nitrogen flow. The morphology and particle size of the products were investigated using a JEOL/EO JSM 6060 scanning electron microscope (SEM) operating at 20 kV. After sample pretreatment for 3 h at 80 °C, the specific surface areas of the samples were determined by nitrogen adsorption-desorption using a Micrometrics TriStar II 3020. The crystallinity was evaluated by X-ray diffraction (XRD) on a Siemens D500 diffractometer with Cu Ka radiation (l = 1.54056 Å). The nickel content of the solids was determined by flame atomic absorption spectrometry (FAAS). The analysis was performed on a Perkin Elmer A atomic absorption spectrometer with a hollow nickel cathode lamp ($\lambda = 232$ nm) and air-acetylene flame (10 L/min: 2.5 L/min). The samples were prepared by treating 15 mg of the heterogenized complex with 2 mL of HCl, 6 mL of HNO₃ and 5 mL of HF, adding the mixture to teflon autoclaves and subsequently using a digester for 24 h at 150 °C. After cooling, the samples were diluted to 50 mL.

2.1. Ligands

As previously published [31], 1,5-*bis*(phenyl)-pentanediimine, **A**, was synthesized by reacting acetylacetone and aniline in the presence of HCl as the catalyst (Figure 1). A

mixture of 10.3 mL of acetylacetone (100 mmol) and 18.0 mL of aniline (200 mmol) was placed in a 250 mL Schlenk tube in an ice bath, and 8.3 mL of hydrochloric acid was added slowly under stirring. A yellow-brown solution was formed. After 12 h under stirring, the reaction mixture was filtered, and the solid was washed with hexane. The solid was dissolved by the addition of 8 mL of CH_2Cl_2 , 50 mL of H_2O and 20 mL of triethylamine. The aqueous phase was extracted with ether and combined with the organic phase. After the solvent was evaporated under reduced pressure, the crude product was recrystallized with methanol, giving 8.07 g (32.2 mmol) of ligand **A** in a 32 % yield.

Ligands **B**, 1,5-*bis*(2,6-dimethylphenyl)-2,4-pentanediimine, and **C**, 1,5-*bis*(2,4,6trimethylphenyl)-2,4-pentanediimine, were similarly synthesized, but *p*-toluenesulfonic acid was used as the catalyst [32]. For ligand **B**, 4.4 mL (42.8 mmol) of acetylacetone, 11.1 mL of 2,4-dimethylaniline (89.9 mmol) and 42.8 mmol of *p*-toluenesulfonic acid in 100 mL of benzene were added to a Schlenk tube. For ligand **C**, 5.7 mL (55.5 mmol) of acetylacetone, 16.4 mL (116.6 mmol) of 2,4,6-trimethylaniline and 55.5 mmol of *p*toluenesulfonic acid in 100 mL of benzene were added to a Schlenk tube. In both cases, the suspension was refluxed for 24 h, and the water formed was removed using the Dean-Stark apparatus. The solvent was removed under reduced pressure. Then, 60 mL of CH₂Cl₂ and 80 mL of a saturated solution of sodium carbonate were added. The aqueous phase was extracted with CH₂Cl₂. After the solvent was evaporated under reduced pressure, the solids were recrystallized with methanol to give 35.5 mmol of **B** and 39.5 mmol of **C**, which corresponded to 83 % and 92 % yields, respectively.

INSERT FIGURE 1

The results from the ¹H NMR, IR, UV and CHN analyses of the ligands are listed below.

(A) ¹H NMR δ (ppm): 12.72 (s, 1H, N-H), 7.30 (t, 4H, J = 7.8 Hz, *m*-ArH), 7.06 (t, 2H, J=7.5 Hz, *p*-ArH), 6.97 (d, 4H, J=7.8 Hz, *o*-ArH), 4.89 (s, 1H, β -CH), 2.02 (s, 6H, α -CH₃). IR: C=N 1555 cm⁻¹. UV: 305 and 380 nm. CHN Calcd. for C₁₇H₁₈N₂: C = 81.56 %, H = 7.25 %, N = 11.19 %; Found: C = 81.11 %, H = 7.29 %, N = 11.05 %. (**B**) ¹H NMR δ (ppm): 12.20 (s, 1H, N-H), 7.03-6.94 (m, 6H, *m*-ArH+, *p*-ArH), 4.88 (s, 1H, β -CH), 2.16 (12H, s, *o*-CH₃ Ar), 1.69 (s, 6H, α -CH₃). IR: C=N 1545 cm⁻¹. UV: 289 and 353 nm. CHN Calcd. for C₂₁H₂₆N₂: C = 82.31 %, H = 8.55 %, N = 9.14 %; Found: C = 81.88 %, H = 8.82 %, N = 9.17 %.

(C) ¹H NMR δ (ppm): 12.15 (s, 1H, N-H), 6.85 (s, 4H, *m*-ArH), 4.85 (s, 1H, β -CH), 2.25 (6H, s, *p*-CH₃ Ar), 2.11 (s, 12H, *o*-CH₃ Ar), 1.68 (s, 6H, α -CH₃). IR: C=N 1550 cm⁻¹. UV: 286 and 365 nm. CHN Calcd. for C₂₃H₃₀N₂: C = 82.59 %, H = 9.04 %, N = 8.37 %; Found: C = 82.68 %, H = 9.40 %, N = 8.37 %.

2.2 Nickel-β-diimine complexes

The nickel- β -diimine complexes corresponding to ligands A-C were obtained by reacting Ni(MeCN)₂Br₂ with the corresponding ligands as shown in Figure 2.

INSERT FIGURE 2

In a Schlenk tube, a solution of 6 mmol of the ligand dissolved in 20 mL of CH_2Cl_2 was added to a suspension of 3.06 g (10.2 mmol) of Ni(MeCN)₂Br₂ in 40 mL of CH_2Cl_2 and maintained under stirring for 5 days at room temperature. The mixture was filtered, and the solvent was removed under reduced pressure, resulting in a purple solid with 20-32 % yield.

The Ni-A complex gives IR: 1594 cm⁻¹ (vC=N); CHN Calcd. for $C_{17}H_{18}Br_2N_2Ni$: C = 43.55 %, H = 3.87 %, N = 5.98 %; Found: C = 45.30 %, H = 3.98 %, N = 5.90 %. The Ni-B complex gives IR: 1620 cm⁻¹ (vC=N); CHN Calcd. for $C_{21}H_{26}Br_2N_2Ni$: C = 48.05 %, H = 4.99 %, N = 5.34 %; Found: C = 48.05 %, H = 5.05 %, N = 5.27 %. The Ni-C complex gives IR: 1619 cm⁻¹ (vC=N); CHN Calcd. for $C_{23}H_{30}Br_2N_2Ni$: C = 49.96 %, H = 5.47 %, N = 5.07 %; Found: C = 50.36 %, H = 5.52 %, N = 5.12 %.

2.3 Hybrid β-diimine/silica xerogels and nickel-β-diiminesil/silica

The xerogel syntheses were carried out according to procedures adapted from the literature [25, 30] for the sol-gel method.

Ligands **A**, **B** and **C** (6 mmol) were activated with sodium hydride (0.21 g, 9 mmol) in 20 mL of CH_2Cl_2 for 30 min at 35 °C (step **1** in Figure 3). Then, a solution of 3chloropropyltrimethoxysilane (CPTMS) (1.1 mL, 6 mmol) in 5 mL of a toluene and THF mixture was added. The mixture was stirred under argon and maintained under reflux for 3 h. The solution was then cooled and centrifuged at 5000 rpm for 20 min, and the supernatant was used as the sol–gel chelating organic precursor in the gel formation process (step **2**, Figure 3). Afterwards, tetraethylorthosilicate (TEOS) (50 mL), ethanol (50 mL), water (16 mL) and HF (1 mL) were added under stirring to the precursor solution. The gelation occurs by the fluoride catalytic process at pH 4. The mixture was stored for a week for gelation and solvent evaporation. The resulting xerogel was washed using 20 mL of each of the following solvents: toluene, THF, CH_2Cl_2 , ethanol, water and diethyl-ether. The xerogel was dried for 4 h in an oven at 60 °C (step **3** in Figure 3). The resulting hybrid silicas were named **HA**, **HB** and **HC** for hybrid silica containing the corresponding ligands.

To remove residual moisture, the solid phase was dried in vacuum (10^{-2} mbar) at 80 °C for 24 h. Then, a suspension of 1 mole of Ni(CH₃CN)₂Br₂ [33] per mole of ligand is dissolved in 20 mL of CH₂Cl₂, added to 1.0 g of β -diiminesil/silica and maintained under stirring for 5 days at room temperature. The solid phase was filtered and extensively washed with CH₃CN (4 aliquots of 30 mL). The solid phase, Ni(II)-(ligand)- β -diiminesil/silica (step 4, Figure 3), was dried at 60 °C for 1 h. The heterogenized complexes were named Ni-HA, Ni-HB and Ni-HC when obtained from the HA, HB and HC hybrid silicas, respectively.

INSERT FIGURE 3

2.4 Ethylene-oligomerization runs

Ethylene-oligomerization experiments were carried out in a 450 mL Parr stainless steel autoclave equipped with magnetically driven mechanical stirring, a thermocouple and a pressure gauge. The reaction temperature (10) was controlled with a thermostatic bath.

In a typical homogeneous reaction run, 20 μ mol of the catalytic precursor and 60 mL of toluene were added to the reactor under argon, followed by the addition of a solution of EASC. The reactor was pressurized with ethylene, and the temperature was adjusted to 10 ° C with a thermostatic bath circulation. The Al/Ni molar ratios varied from 30 to 200, and the ethylene pressure ranged from 5 atm to 15 atm. After 30 min, the reaction was stopped, and the mixture was cooled to -30 °C and analyzed immediately by gas chromatography.

Heterogeneous-medium runs were performed, and the results were compared to the results obtained with the homogeneous-phase complex. In a typical heterogeneous-medium experiment, the reactor was charged with a suspension of the desired catalytic precursor containing 6.5 μ mol or 20 μ mol of nickel and 60 mL of toluene saturated with ethylene, and the temperature was adjusted to 10 $^{\circ}$ C. The pressure was raised to 15 atm under continuous stirring. The amount of alkylaluminum co-catalysts introduced into the reactor was calculated to obtain an aluminum to nickel molar ratio (Al/Ni) between 100 and 1200. After 30 min, the reaction was stopped, and the mixture was cooled and analyzed immediately by gas chromatography.

Recycle experiments were carried out in a 100 mL double-walled glass reactor containing a magnetic stirring bar with a constant supply of neat gaseous ethylene at 5 atm and a thermocouple to measure the temperature. The reaction temperature was regulated to 10 °C by an external-circulation ethanol bath. In a typical experiment, the reactor was charged with a solution of the desired catalytic precursor (20 µmol) in 50 mL of toluene saturated with ethylene. The reactor was purged with ethylene, and the alkylaluminum solution is added in amounts calculated to obtain an aluminum to nickel molar ratio (Al/Ni) of 200. After 30 min, the reaction was stopped, and the mixture was cooled and analyzed by gas chromatography. After the first reaction, the products were removed from the reactor through a cannula and collected at -20 °C. Catalyst recycling was accomplished by adding another 50 mL of toluene and continuing the reaction.

In all cases, chromatographic analyses were performed on a Varian 3400CX gas chromatograph equipped with a Petrocol DH capillary column (methyl silicone, 100 m long, 0.25 mm ID, 0.5 μ m film thickness). Analysis conditions were 36 °C for 15 min, followed by heating at a rate of 5 °C/min up to 250 °C. The products were identified by the method of co-injection of standards, and cyclohexane was used as the internal standard for

quantification. The TOF values, defined as moles of converted ethylene per mole of precatalyst per reaction time (in h), show a variation of ± 12 %, as determined by at least three independent experiments performed at each condition.

3. Results and discussion

The formation of the Ni-A, Ni-B and Ni-C complexes from the corresponding parent ligands A, B and C is accompanied by an enhancement of the infrared C=N stretching frequencies by 36, 41 and 25 cm⁻¹, respectively. Figure 4 gives the IR spectrum of the Ni-C complex as an example.

INSERT FIGURE 4

The energy associated with the CN vibrations of the imine ligands is expected to decrease upon simple metal complexation. The observed energy increase indicates a change in the conjugated structure of the free ligand to a non-conjugated structure of the ligand when coordinated to the metal, giving the corresponding Ni- β -diimine complexes.

The measured elemental compositions of the homogeneous complexes are consistent with the calculated values for **Ni-B** and **Ni-C**; however, a higher %C is observed for **Ni-A**, most likely due to the presence of residual ligands.

The synthesis of the **HA**, **HB** and **HC** hybrid silicas containing the corresponding ligands in their composition is performed in three steps. The starting point is the activation of the ligands with NaH to form the sodium salt, which is monitored by the release of the H_2 formed (step **1** of Figure 3). The synthesis of the organic precursor by reaction with CPTMS follows (step **2** of Figure 3), and finally, the polycondensation with TEOS in presence of HF completes the procedure, forming the hybrid silica (step **3** of Figure 3). The incorporation of the organic material is monitored by elemental analysis.

The amount of ligand incorporated into the silica and the ligand:Si ratio is calculated from the nitrogen content obtained by elemental analysis as shown in Table 1.

The organic matter is incorporated into the support at 20-40 %, and the ligand:Si molar ratio is between 1:100 and 1:180. The hybrid material produced with ligand C has low organic content (**HC**), most likely due to the steric hindrance of ligand C.

INSERT TABLE 1

Table 1. Characteristics of the hybrid β -diimine/silica xerogels and corresponding nickel complexes.

Ligand	Organic content	Ligand:Si	Specific area ^b	Heterog.	Nickel content ^b
	mmol/g		m²/g	complex	mmol/g
HA	0.128	1:120	176	Ni-HA	0.110
HB	0.150	1:100	206	Ni-HB	0.187
HC	0.080	1:180	191	Ni-HC	0.025
\mathbf{W}^{a}	0.000	0	Nd	"Ni"-W	0.000

Reaction conditions: 6 mmol ligand, 225 mmol TEOS, 1 mL HF.^a Control: silica obtained without addition of the ligand.

^b Determined by BET.

Figure 5 shows the infrared spectra of the **HA**, **HB** and **HC** hybrid silicas. The control silica **W** shows the silica overtones bands at 1984 and 1877 cm⁻¹. The hybrid silica contains two components: an inorganic one and an organic one. The organic component can be identified by the deformation bands of the N-H group at 1540 cm⁻¹. The band related to the stretching of the C=N group is superimposed on the H-O-H deformation band appearing at 1625 cm⁻¹, which originates from the adsorbed water in the silica.

INSERT FIGURE 5

The electronic spectra of the free ligands show two bands at 305 nm and 380 nm for ligand **A**, 289 nm and 353 nm for ligand **B** and 286 nm and 365 nm for ligand **C**. The spectra of the hybrid silicas exhibit only one band at 320 nm for the **HA** hybrid silica, 318

nm for the **HB** hybrid silica and 320 nm for the **HC** hybrid silica. These bands are shifted from 305 nm to 320 nm in the **HA** hybrid material, from 286 nm to 318 nm in **HB** and from 289 nm to 320 nm in **HC** when the corresponding free ligands are compared to the hybrid silicas. This behavior can be attributed to the fact that in the hybrid material, the ligand is trapped, and the electronic transitions are less energetic than when the ligand is in the free state. The bands at 380 nm for the **HA** hybrid material, at 353 nm for **HB** and 365 nm for **HC** disappear when the ligand isn't free, which can be attributed to the lower mobility of the intermolecular hydrogen bond when supported in the hybrid material.

The specific areas of the hybrid silicas were calculated by the BET method, giving 176 m²/g for the **HA** hybrid silica, 206 m²/g for the **HB** hybrid silica and 191 m²/g for the **HC** hybrid silica. These results are similar to those reported by Brinker and Scherer [34] for silica gel. The isotherms are type IV [35], characteristic of mesoporous materials, and show type *H3* hysteresis, which indicates the presence of plate-like particles that give rise to slit-shaped pores.

INSERT FIGURE 6

The X-ray diffractograms of the xerogels showed only a broad peak at 2θ between 16° and 26°, suggesting that the hybrid materials are basically amorphous.

The TGA analysis is more instructive and shows a decomposition temperature of 260 °C for the free ligands, which increases to 400 °C when the ligands are anchored in the inorganic support. This increase in decomposition temperature demonstrates the significant increase in the stability of these ligands upon immobilization on the inorganic support.

The nickel complexes on hybrid silica corresponding to Ni-A, Ni-B and Ni-C were prepared by reacting the corresponding hybrid silica with a solution of nickel bromide. The amount of heterogenized nickel was determined by FAAS and is shown in the last column of Table 1. In the case of ligand A, the amount of nickel incorporated into the Ni-HA catalyst (0.11 mmol/g) is very close to the amount of ligand present in the parent HA silica (0.12 mmol/g). In the Ni-HB catalyst, the amount of nickel incorporated (0.187 mmol/g) is greater than the amount of ligand present in the HB silica (0.15 mmol/g), indicating the presence of Ni species deposited on the silica surface in addition to those complexed with the heterogenized ligand. In the case of the **Ni-HC** catalyst, the amount of incorporated nickel (0.025 mmol/g) was lower than the amount of ligand present in the **HC** silica, most likely due to the steric hindrance of the ligand, which decreases the metal's access to the binding site and thus limits its incorporation into the catalyst.

Oligomerization runs

The Ni-A, Ni-B and Ni-C nickel complexes have been used as catalysts in combination with ethylaluminum sesquichloride, EASC, for the oligomerization of ethylene. The Ni-A, Ni-B and Ni-C complexes showed activity for ethylene oligomerization, and their performance is affected by the catalyst structure and the reaction conditions. The effects of the nickel precursor structure, amount of alkylaluminum compound (Al/Ni ratio) and ethylene pressure on the activity and selectivity for ethylene oligomerization are shown in Table 2.

Entry	Complex	Pressure	Al/Ni	TOF	\mathbf{S}_{C_4}	α- C ₄	$\mathbf{S}_{\mathbf{C}_6}$	S_{C_8} +
		(atm)		$(10^3 h^{-1})$	(%)	(%)	(%)	(%)
1	Ni-A	15	100	210	78	32	20	2
2	Ni-B	15	100	18.3	97	87	3	-
3	Ni-C	15	100	18.7	96	87	4	-
4	Ni-C	15	30	4.3	94	93	6	-
5	Ni-C	15	50	6.1	100	95	-	-
6	Ni-C	15	200	16.5	97	91	3	-
7	Ni-C	5	100	5.4	99	93	1	-
8	Ni-C	10	100	9.7	97	90	3	-

Table 2. Ethylene oligomerization results for nickel- β -diimine catalysts in the homogeneous phase.

Complex: 20 μ mol, T = 10 °C, reaction time = 0.5 h, solvent = toluene (60 mL), co-catalyst = EASC.

The Ni-A complex, which contains a phenyl ring without substituents, shows the highest activity (210 x 10^3 h⁻¹) with good selectivity towards C₄ products (78 %). The Ni-B and Ni-C complexes show lower activities than Ni-A but greater selectivity towards C₄

products (96-97 %). These results suggest that the steric hindrance of the methyl groups is responsible for the decrease in ethylene accessibility and consequently for the observed decrease in the reaction activity.

The **Ni-C** complex was chosen for optimization of the reaction parameters for the oligomerization tests.

Initially, the influence of the Al/Ni ratio on the activity and the selectivity of the catalyst was evaluated. The activity of the catalyst increases continuously with the Al/Ni ratio up to a value of 100 (entries 3, 4 and 5 in Table 2), a condition in which the maximum activation of the **Ni-C** complex is attained. A further increase in the amount of co-catalyst up to Al/Ni = 200 (entry 6) decreases the activity of the catalyst, most likely due to catalyst decomposition and the corresponding reduction in the number of active species.

The activity increases linearly with the ethylene pressure (as shown by entries 5, 7 and 8 in Table 2), indicating a first-order dependence in accordance with a Cossee-Arlmann chain-growth mechanism [36].

These observations suggest that the activity trends observed in Table 2 for the Ni-A, Ni-B and Ni-C catalysts are related to electronic effects instead of steric effects. The larger electronic effect of the ligand compared to its steric hindrance is also consistent with the results for α -keto- β -diimine nickel catalysts for ethylene polymerization [37, 38].

The selectivities of the Ni-B and Ni-C catalysts for C_4 products and 1-butene are very similar. The Ni-A catalyst exhibits much low selectivities compared to Ni-B and Ni-C. The decrease in the C_4 selectivity of the Ni-A catalyst can be attributed to a consequence of the co-oligomerization reaction of ethylene with the olefin reaction products of this catalyst (produced after 1-butene insertion at the metal-hydride bond), which has already been observed for cobalt and iron catalysts [39].

Comparison of the results described in the literature with those for the nickel complexes with β -diimine ligands herein described shows that the catalysts in this paper have similar activities but much higher selectivities towards C₄ products and, more importantly, towards α -olefins [40-42]. Zhang [43] used β -diimine complexes for ethylene oligo/polymerization with MAO as an activator and obtained oligomers in the range from

 C_4 to C_8 and high molecular weight polyethylene with an activity of approximately 18 x 10^3 h⁻¹. Li [44] studied the effect of CF₃ substituents on the electrophilicity of catalysts used for ethylene oligo/polymerization. In this study, MAO was used as an activator, and oligomers ranging from C_4 to C_8 were obtained simultaneously with polyethylene with an activity of 350 x 10^3 h⁻¹.

Oligomerization using EASC like co-catalyst were very active. The EASC is a known choice was based at literature. Eberhardt at al described EASC like the most efficient activator to their nickel complex because this co-catalyst is both Lewis acid and alkylating agent. [45].

The reactions using these nickel complexes heterogenized in hybrid silica were performed at similar conditions to those used for the homogeneous-phase runs to compare their behaviors. Different Al/Ni ratios (100 to 1200) and different amounts of catalyst (6.5 μ mol and 20 μ mol) have been tested, and the results are shown in Table 3.

Entry	Complex	μmol	Al/Ni	TOF	α -C ₄ ^a
				$(10^3 \cdot h^{-1})$	(%)
1			100	1.8	92
2	Ni-HA	20	200	2.2	96
3			400	12.8	91
4			100	2.5	94
5	Ni-HB	20	200	4.3	100
6			400	2.3	100
7			300	10.3	95
8	Ni-HC	6.5	600	13.8	93
9			1200	13.3	96
10 ^b	W		с	0	-

Table 3. Results of ethylene oligomerization by heterogenized nickel- β -diimine/silica complexes.

Complex: T = 10 °C, pressure = 15 atm, reaction time = 0.5 h, solvent = toluene (60 mL), co-catalyst = EASC. ^a SC₄ = 100 %. ^b Silica synthesized without the presence of an organic precursor. ^c Same volume as entry 2.

The mechanism of the catalytic reaction can be described as involving an alkylnickel species, **2**, (obtained by alkylation with the EASC co-catalyst) or a nickel-hydride species, **5**, (obtained by ethylene insertion at the nickel-carbon bond on species **2** followed by β -elimination and 1-butene descoordination). Both species are formed from the **Ni-A**, **Ni-B**, **Ni-C**, **Ni-HA**, **Ni-HB** or **Ni-HC** complexes (Figure 7). Ethylene insertion on species **2** gives **3**. β -elimination on species **3** gives **4**. The intermediate **4** can give 1-butene via dissociation or species **6** via 1-butene insertion at the nickel-hydride bond. Compound **6** can give 2-butene from β -elimination associated with the dissociation reaction.

INSERT FIGURE 7

The three nickel- β -diimine/silica complexes have the same selectivity for C₄ fraction (100 %) and similar selectivities for α -C₄ (above 90 %).

The best activities for the Ni-HA, Ni-HB and Ni-HC complexes were obtained with Al/Ni ratios of 400, 200 and 600, respectively. The Ni-HC catalyst showed the best activity (13.8 x 10^3 h⁻¹) among the catalysts tested. Busico et al. [46] demonstrated that a lower catalyst concentration coupled with a greater amount of active species available for olefins provides higher catalytic activity. The Ni-HA catalyst showed a higher activity of 12.8 x 10^3 h⁻¹ compared to the Ni-HB catalyst, which had an activity of 4.3 x 10^3 h⁻¹.

Comparing the results for the homogeneous nickel- β -diimine complex in entries 1, 2 and 3 of Table 2 with the results for the heterogenized nickel- β -diimine/silica complex shows that heterogenization is accompanied by a considerable decrease in catalytic activity. This fact can be explained by the limited accessibility of the metal centers to the olefin in the heterogenized complexes, which leads to a smaller number of available active species and lower catalytic activity as described in other heterogenized systems [47,48]. It was also noted that the heterogenized complexes required a greater amount of the alkylaluminum activator than the homogeneous complex. This result is most likely due to the presence of hydroxyl groups on the support surface of the heterogenized catalyst, which consume part of the alkylaluminum. The heterogenized complexes show better

selectivities for the C_4 and α - C_4 fractions than the homogeneous complexes. The addition of the silica catalyst support also acts to sterically hinder the formation of internal olefins.

Entry 10 in Table 3 presents the results of the reaction with the material without organic matter (White) **W**, which shows no catalytic activity.

Figure 8 presents the results for the recycle reactions using the heterogenized Ni-HA catalyst. The catalyst shows a decrease in activity for the first and second recycles, but the selectivity for α -C₄ is maintained.

INSERT FIGURE 8

4. Conclusions

Nickel- β -diimine complexes and nickel- β -diimine/silica are active in ethylene oligomerization. The homogeneous-phase reaction shows the strong influence of the ligand structure on the formation of the products. The best results in oligomerization activity and selectivity for the homogeneous complexes are obtained with an Al/Ni molar ratio of 100. An excess of alkylaluminum results in a decrease in the activity, and an increase in the ethylene pressure shows first-order kinetics and affords the best activities without changing the selectivity. The **Ni-A** complex has an activity of approximately 210.0 x 10³ h⁻¹, and the **Ni-B** and **Ni-C** complexes have activities of 18.3 x 10³ h⁻¹ and 18.7 x 10³ h⁻¹, respectively. The decrease in activity for these catalysts is most likely due to the higher steric hindrance of the methyl groups on the ligands, which produce catalysts with high selectivities for C₄ products (>95 %) and α -olefins (>85 %).

The hybrid silicas were synthesized by the sol-gel method, which resulted in good incorporation of the organic phase. The β -diimine/silica xerogels are thermally stable. It was possible to incorporate nickel into the resulting hybrid silica complex to form heterogenized nickel- β -diimine/silica.

The heterogeneous catalysts had lower activity than their homogeneous analogues, but they demonstrated much better selectivity for C_4 fractions (100 %) and for α - C_4

fractions (>90 %). It is observed that a smaller amount of the catalyst precursor was needed to obtain a higher catalytic activity. The silica support also prevents the formation of internal olefins.

Recycle reactions were performed with the heterogenized **Ni-A** complex, which was shown to be active and selective in the recycle reactions and is therefore promising for large-scale use.

5. Acknowledgements

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FIGURE ABSTRACT





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Figure 8. Results of the Ni-A catalyst recycle reactions.

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Ligand	Organic content	Ligand:Si	Specific area ^b	Heterog.	Nickel content ^b
	mmol/g		m ² /g	complex	mmol/g
HA	0.128	1:120	176	Ni-HA	0.110
HB	0.150	1:100	206	Ni-HB	0.187
НС	0.080	1:180	191	Ni-HC	0.025
\mathbf{W}^{a}	0.000	0	Nd	"Ni"-W	0.000

Table	1.	Characteristics	of	the	hybrid	β-diimine/silica	xerogels	and	corresponding
nickel	cor	nplexes.							

Reaction conditions: 6 mmol ligand, 225 mmol TEOS, 1 mL HF. ^a Control: silica obtained without addition of the ligand.

^b Determined by BET.

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Table(s)

ACCEPTED MANUSCRIPT

Entry	Complex	Pressure	Al/Ni	TOF	\mathbf{S}_{C_4}	α- C ₄	\mathbf{SC}_{6}	S_{C_8} +
		(atm)		(10^3h^{-1})	(%)	(%)	(%)	(%)
1	Ni-A	15	100	210	78	32	20	2
2	Ni-B	15	100	18.3	97	87	3	
3	Ni-C	15	100	18.7	96	87	4	G
4	Ni-C	15	30	4.3	94	93	6	K
5	Ni-C	15	50	6.1	100	95	C -	-
6	Ni-C	15	200	16.5	97	91	3	-
7	Ni-C	5	100	5.4	99	93	1	-
8	Ni-C	10	100	9.7	97	90	3	-

Table 2. Ethylene oligomerization results for nickel- β -diimine catalysts in the homogeneous phase.

Complex: 20 μ mol, T = 10 °C, reaction time = 0.5 h, solvent = toluene (60 mL), co-catalyst = EASC.

ACCEPTED MANUSCRIPT

Entry	Complex	μmol	Al/Ni	TOF	α -C ₄ ^a
				$(10^3 \cdot h^{-1})$	(%)
1			100	1.8	92
2	Ni-HA	20	200	2.2	96
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6			400	2.3	100
7			300	10.3	95
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9			1200	13.3	96
10 ^b	W		с	0	-

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Complex: T = 10 °C, pressure = 15 atm, reaction time = 0.5 h, solvent = toluene (60 mL), co-catalyst = EASC. ^a SC₄ = 100 %. ^b Silica synthesized without the presence of an organic precursor. ^c Same volume as entry 2.