



Heterogeneous complexes of nickel MCM-41 with β -diimine ligands: Applications in olefin oligomerization



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ABSTRACT

The β -diimine ligands 2-(phenyl)amine-4-(phenyl)imine-2-pentene and 2-(2,6-dimethylphenyl)amine-4-(2,6-dimethylphenyl)imine-2-pentene were combined with the alkoxy silane group chloropropyltrimethoxysilane (CPTMS) and covalently anchored to a mesoporous MCM-41 support; they were ordered via interactions with the silanols of the silica matrix and complexed with nickel. The complexes were synthesized for use in ethylene and propylene oligomerization and for comparing the results of homogeneous and heterogeneous systems. The support was first synthesized, calcined, anchored to the ligand, and then, complexed with nickel. These materials were characterized using various techniques, such as ¹H, ¹³C, and ²⁹Si NMR, small angle XRD, thermogravimetric analysis, adsorption isotherms, transmission electron microscopy, and flame atomic absorption spectroscopy, to confirm the success of the synthesis. Both homogeneous and heterogeneous complexes are active and selective for the reactions of ethylene and propylene oligomerization.

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1. Introduction

The development of materials and methods for catalytic oligomerization of light olefins to give α -olefins, such as 1-butene and 1-hexene, is an important topic in the chemical industry [1]. In the current climate and for the environmental vision of the world, developing systems that are more efficient, economically viable, and less harmful to the environment is very important. In this context, heterogeneous systems and anchoring of homogeneous catalytic complexes on supports, such as alumina and silica [2], are very promising methods for reducing the use of organic solvents in the easy separation of the reaction medium, thus reducing the costs and environmental impact [3].

The most important heterogeneous catalysts use nickel for ethylene oligomerization and are based on inorganic porous materials. The major methods for the preparation of heterogeneous nickel catalysts for oligomerization include NiO or NiSO₄ on various inorganic supports, Ni-exchanged zeolites, mesoporous materials (MCM-41, Al-MCM-41), sulfated alumina, and silica–alumina [4–7]. However, when nickel complexes were heterogenized on inor-

ganic supports (SiO₂ or Al₂O₃), a decrease in activity occurred in some cases, and increases in selectivity and catalyst stability were often observed in ethylene oligomerization reactions [8–10].

Nickel complexes are most commonly used for oligomerization reactions in homogeneous media because of their high activity and ability to form specific products. Therefore, they are highly successful both from an academic standpoint and in the industry, resulting in their use in various industrial processes [11–13]. The commercial oligomerization of ethylene is predominantly performed using transition metal catalysts that produce a wide distribution of linear α -olefins, which are used in polymerization and the preparation of a variety of economically important compounds, such as detergents, synthetic lubricants, plasticizers, and alcohols [1]. Propylene has been less well studied than ethylene as an active and selective catalyst for α -olefins; there are also problems with it regarding its dimer requirements and in obtaining products with the desired regioselectivity [14].

Highly active nickel complexes with diimine ligands for ethylene oligomerization or polymerization were introduced by Brookhart et al. [15–18]. After that, significant effort was put toward studying the effects of the structures of the ligands on the catalytic properties of the metal complexes involved in the oligo/polymerization [19–22]. β -diimines and β -diiminates have been studied as ligands for transition metal compounds [23,24]. Some ligands, such

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¹ In memoriam.

as β -diimines, are easy to prepare and have several attractive properties, including tunable electronic and steric parameters [22]. In the case of β -diimine ligands, the presence of acidic protons in the α position facilitates their anchoring via covalent bonding to the inorganic supports.

Homogeneous catalysts usually contain uniform and well-defined active sites, which lead to high activities and reproducible selectivities. However, the major drawback of 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 [25–28].

In the 1990s, a new family of porous materials, which present a system of well-defined mesopore sizes with a regular spatial arrangement, was discovered by scientists at Mobil [29]. This family is called M41S and is composed of three types of phases; one of this materials was called MCM-41. Mesoporous materials of the MCM-41 type are very interesting because they have ordered arrays of uniform channels, a high surface area, thermal and chemical stability, and shape selectivity. These materials have a large number of hydroxyl groups, which provide the necessary qualities for modification of the internal and external surfaces, and the possibility of the self-assembly of molecules; these properties provide excellent chemical aggregation via covalent complexation with homogeneous media [30]. The synthesis of mesoporous materials modified with reactive functional groups, such as amines, aldehydes, nitriles, phenyls, thiols [31,32], modifying organic groups (functional ligands), or organometallic complexes with silanol groups (CPTMS and CPTES), for anchoring via covalent bonding, has been well studied with promising results observed in the last decade [3,30]. These systems allow anchoring via covalent bonding between the silanol groups of the organic functional groups and the Si–OH groups of the mesoporous materials or between the functional groups of the modified mesoporous materials and organic groups of interest.

There are studies that use homogeneous nickel complexes of β -diimines for oligomerization of olefins [8,33–36]; however, there are no reports of studies using anchoring via covalent bonds between nickel complexes, β -diimines, and ordered mesoporous materials for the oligomerization of ethylene and propylene.

The objective of this study was to investigate the potential for developing new nickel complexes heterogenized on mesoporous materials via anchoring with covalent bonds between the MCM-41 mesoporous support and nickel complexes with β -diimine ligands, attempting to produce catalyst complexes that are active and selective for the oligomerization of olefins (ethylene and propylene).

2. Experimental section

All experiments were performed under an argon atmosphere using standard Schlenk techniques. The solvents were deoxygenated by refluxing over appropriate drying agents (toluene and ethyl ether on sodium benzophenone and dichloromethane and acetonitrile on phosphorous pentoxide) under argon and distilled immediately prior to use. Methanol and tetrahydrofuran (THF) were used without further purification. Aniline, 2,6-dimethylaniline, and hexadecyltrimethylammonium bromide (CTABr) were purchased from Sigma–Aldrich and distilled under reduced pressure prior to use. 3-chloropropyltrimethoxysilane (CPTMS), sodium aluminate, sodium hydroxide, tetramethyl ammonium hydroxide (TMAOH), sodium hydride (NaH), and anhydrous nickel bromide (NiBr_2) were purchased from Sigma–Aldrich. Silica Aerosil 200 was purchased from Degussa. *p*-Toluenesulfonic acid (Vetec) was distilled on toluene using the Dean–Stark technique. Sodium carbonate was purchased

from Vetec and used without further purification. Ethylaluminum sesquichloride ($\text{Al}_2\text{Et}_3\text{Cl}_3$, EASC) was supplied by Akzo Nobel and used with toluene dilution (10%). The solids were dried under reduced pressure.

2.1. Characterization techniques

Elemental analyses were performed using a Perkin Elmer M CHN Analyzer 2400. The liquid ^{13}C NMR analyses were performed using a Varian Inova 400 MHz solubilized in deuterated chloroform (CDCl_3). The ^{13}C and ^{29}Si CP-MAS-NMR analyses were performed using an Agilent 500 MHz spectrometer model DD2 operated at 125.7 MHz for ^{13}C and 99.3 MHz for ^{29}Si using adamantane as a reference material for peak assignments. The solid NMR conditions are an acquisition time of 7 ms and a delay of 10 s with a rotation of 10 kHz to ^{13}C and an acquisition time of 9 ms and a delay of 5 s with a rotation of 5 kHz to ^{29}Si . Thermogravimetric analyses were performed on a TA Instrument 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 an EVO50, Carl Zeiss scanning electron microscope (SEM) operating at 30 kV. For the TEM analysis, a JEOL JEM 2010 transmission model was used with an acceleration voltage of 200 kV. After sample pretreatment for 12 h at 90 °C, the specific surface areas of the samples were determined via nitrogen adsorption-desorption using a Micrometrics TriStar II 3020. X-ray diffraction analyses were performed on a Bruker D2 Phaser using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) in the range $2\theta = 1^\circ\text{--}8^\circ$ using slits of 0.1 and 3 nm. The nickel content of the solids was determined via flame atomic absorption spectrometry (FAAS). The analysis was performed using a Perkin Elmer A atomic absorption spectrometer with a hollow nickel cathode lamp ($\lambda = 232 \text{ nm}$) and air–acetylene flame (10 L/min: 2.5 L/min). The samples were prepared by treating 50 mg of the heterogeneous complex with 2 mL of HCl, 6 mL of HNO_3 , 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.

2.2. Synthesis of **L1** and **L2** ligands and homogeneous **C1** and **C2** nickel complexes

The syntheses and characterization of ligands **L1** = 2-(phenyl)amine-4-(phenyl)imine-2-pentene and **L2** = 2-(2,6-dimethylphenyl)amine-4-(2,6-dimethylphenyl)imine-2-pentene and their corresponding nickel complexes **C1** = dibromo(*N,N*-bis(phenyl)-2,4-pentanediiimine)nickel(II) and **C2** = dibromo(*N,N*-bis(2,4-dimethylphenyl)-2,4-pentanediiimine)nickel(II) were described in a previous work [8].

2.3. Synthesis of MCM-41

The syntheses of mesoporous MCM-41 materials were based on the synthesis described by Corma et al. [36]. The synthesized material has the following molar ratio: 1 SiO_2 :0.1 CTABr:0.25 TMAOH:20 H_2O .

Solution A was added to a plastic beaker under heating at 40 °C and mechanical agitation with 134 g of distilled water and 20 g of CTABr. The solution was stirred for 1 h.

Solution B: In a plastic beaker, 34.6 g of TMAOH 25% and 3.84 g of aerosil silica were added and left under magnetic stirring for 45 min to homogenize the sample.

Subsequently, solution B was added to solution A under mechanical stirring and slowly added to 18.08 g of aerosil silica. The gel formed was left under stirring for 1 h to homogenize the sample (pH = 13). The resulting gel was transferred to 4 stainless steel autoclaves with Teflon slings and placed in a static oven at

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