

Research Note

XAS study of the nickel(α -diimine) catalyst for olefin polymerization

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Abstract

The in situ Ni *K*-edge XAS study of the Ni(α -diimine)Cl₂/methylalumoxane catalyst during 1-decene polymerization indicates the formation of a complex with Ni(II) atoms bonded to C and N atoms as well as a Ni...Cl interaction at ca. 4.02 Å, which suggests the formation of a pentacoordinated nickel complex as the active site. This geometry explains spectroscopic and magnetic properties of the complexes and can play an important role in the polymerization of ethylene by late transition metal catalysts.

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1. Introduction

The nature of the interaction between transition metal complexes and alkylaluminum activators remains a relevant and hitherto unresolved question [1]. The academic and technological importance of olefin polymerization catalyzed by nickel complexes, as used in the Du Pont Versipol process [2], has rekindled interest in understanding this interaction.

When Ni(α -diimine)Cl₂ complexes are activated with alkylaluminum compounds, deeply colored solutions are formed. The UV–visible spectra of these systems have been reported by different groups [3]. For instance, when (1,4-bis(2,6-diisopropylphenyl)-acenaphthenediimine)NiCl₂ (**1**) is mixed with methylalumoxane (MAO) in the presence of ethylene, two bands, at 529 and 704 nm, with molar absorptivities (ϵ) of 2800 and 1840 L mol⁻¹ cm⁻¹, respectively, are present in the spectrum, but if triisobutylaluminum (TiBA) is used, bands at 538 and 709 nm, with molar absorptivities of 1800 and 2730, respectively, are present. Such molar absorptivities are too high to be attributable to *d*–*d* transitions in tetra- or hexa-coordinated Ni(II) complexes. It is well known that octahedral Ni(II) complexes show three moderately intense bands ($\epsilon \approx 10$) and that tetrahedral or

square-planar Ni complexes exhibit one to three absorption bands with ϵ in the range 1 to 150 [4].

The magnetic susceptibilities of these systems give complementary information. Complex **1** has a 2.1 ± 0.1 BM magnetic susceptibility and the system 1/TiBA/ethylene 1.4 ± 0.1 BM, which suggests that the tetrahedral geometry observed for complex **1** changes upon addition of alkylaluminum compounds and deviates from the square-planar geometry. This behavior could be explained by incomplete transformation of **1** into a square-planar complex, but this does not explain the observed UV–visible spectra. These data explain the need for further characterization of the complexes in order to understand the nature of the active species in nickel-catalyzed olefin polymerization reactions.

In this paper, we describe a model for the coordination sphere of the (α -diimine)NiCl₂ olefin polymerization catalyst obtained by the X-ray absorption spectroscopy (XAS) method. This technique gives information about the structural environment of specific elements present even in low amounts, as demonstrated by Corker and Evans in an elegant application of XAS that shows the interactions between nickel and alkylaluminum compounds [5]. The coordination geometry of the nickel species is probed by the X-ray absorption near edge structure (XANES) method and the number and the nature of the nearest-neighbor atoms around the nickel core are calculated from the extended X-ray absorption fine structure (EXAFS) features [6].

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2. Methods

2.1. XAS measurements

XAS measurements at the nickel *K*-edge were performed at the Laboratório Nacional de Luz Síncrotron—LNLS using the XAS beam line [7]. A “channel-cut” Si(111) crystal monochromatized the collimated X-ray beam. The XANES measurements were done using vertical slits of 0.5 mm placed before the monochromator providing an energy resolution of 2.4 eV. The EXAFS measurements were recorded using vertical slits of 1.5 mm. Data were recorded in fluorescence mode, using an ionization chamber and a NaI scintillator. The monochromator was calibrated at the Ni *K*-edge, using a Ni metal foil. The energy step was 0.8 eV in the XANES spectra and 2 eV in the EXAFS spectra; the acquisition time was 2 s/point. Due to the low concentration of nickel in the sample, 15 acquisitions were done and averaged to get a better signal-to-noise ratio.

The EXAFS spectra were analyzed by a standard procedure of data reduction, using the Winxas program [8]: extraction of the EXAFS signal $\chi(k)$, Fourier transformation from 2.5 to 9.4 Å⁻¹ using a Kaiser window. The refinement of the shells was made by using phases and amplitudes derived from the FEFF code [9]. In the fitting procedure, the number of free parameters did not exceed the number of independent data points given by the Nyquist theorem [10].

2.2. Polymerization procedure

The EXAFS polymerization sample was prepared inside a glove box by mixing chlorobenzene, 1-decene ([monomer]/[**1**] = 400), complex **1** (408 ppm), and MAO ([Al]/[**1**] = 10). The sample was mounted on a Teflon sample holder with Mylar windows.

These reaction conditions were chosen to ensure that the XAS experiment was performed with the catalyst operating under reaction conditions in which the conversion of the olefin was limited to 75%, i.e., no total conversion was attained even during long-time acquisition experiments. This leads to expensive experiments, since extremely long acquisition times in the synchrotron ring was used, typically 7 to 8 h.

3. Results and discussion

XANES spectra are dependent on the structural and the chemical environment of the investigated element and its surroundings. The intensities of the preedge and the main-edge features depend on the site symmetry [11]. Preedge features for the *K*-edge correspond to a transition from 1s to 3d states, which is forbidden in a centrosymmetric environment. These transitions are allowed as a result of the metal 3d–4p orbital mixing, metal 3d–ligand 2p orbital overlap, and site distortion. It is expected that the XANES

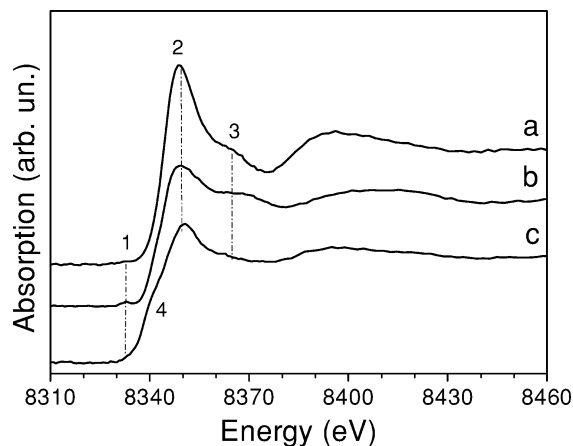


Fig. 1. XANES spectra of the Ni *K*-edge of Ni(acac)₂ (a), nickel(α -diimine)Cl₂ **1** (b), and nickel(α -diimine-Cl₂)/MAO/1-decene (c).

features of a metal in a centrosymmetric site exhibit a weak preedge and an intense main edge, as observed for the octahedral geometry. For a noncentrosymmetric site, an increase in the preedge intensity occurs with a corresponding decrease in the main edge, as is typical for tetrahedral geometries.

The normalized XANES spectra at the Ni *K*-edge for Ni(II)-bearing model compounds are shown in Figs. 1a and 1b. Fig. 1c corresponds to the spectrum obtained during the 1-decene polymerization catalyzed by **1**/MAO. The spectra present features labeled 1 (the preedge), 2 (the main edge), and 3 (a multiple scattering resonance). Feature 3 is related to the geometry of the medium-range structure around the investigated element [12].

In the Ni(acac)₂ complex, the Ni(II) atom is octahedral [13] and the XANES (Fig. 1a) display a low-intensity preedge (1s \rightarrow 3d transition) and a high-intensity main edge (1s \rightarrow 4p transition). For the Ni(α -diimine)Cl₂ complex **1** where the Ni(II) atom is tetrahedral [14], the decrease in intensity of the main edge (feature 2) with a corresponding increase in the intensity of the preedge feature 1 corroborates the changes expected for a noncentrosymmetric site. Furthermore, a square-planar geometry, not shown here, is characterized by a strong preedge assignable to the 1s \rightarrow 4p_z transition [15].

The spectrum of the catalytic system, the mixture of **1**/MAO/1-decene (Fig. 1c), has smothered features, which suggests the presence of a more disordered system. However, it is still possible to distinguish the preedge and the main edge, the heights of which are comparable with the characteristics of Ni(α -diimine)Cl₂ (**1**). In the preedge region a shoulder (Fig. 1, feature 4) appears, indicating a distortion in the coordination shell. The shift in Fig. 1c in the catalytic system compared to the standards indicates a distinct organization around Ni in the catalytic system and in the reference samples.

The clear distinction between 4-, 5-, and 6-coordinated Ni is obtained under high-resolution conditions, by analyzing the dependence of the position and the intensity of the

preedge features [16]. In our case, we can only assert that for the catalytic system, the lower intensity of the main edge compared with the octahedral geometry is an indication of lower coordination at the Ni atom and also that the absence of a high-intensity preedge peak eliminates the possibility of square-planar geometry. This means that the 6- and 4-coordinated square-planar configurations can be excluded. Further information was obtained by EXAFS analysis.

The EXAFS studies were experimentally complicated by the low catalyst concentration and by the fact that the measurements were performed on a liquid sample, which demands very long acquisition times and requires careful choice of the type of olefin and the concentrations of all catalytic system components in order for XAS measurements to be performed during the polymerization reaction (maximum 1-decene conversion of 75%). Even under such conditions, well-defined EXAFS spectra have been obtained, as shown in Fig. 2. The EXAFS signal of the catalyst (Fig. 2a) is dominated by the frequency due to the coordination shell. The shoulders marked by arrows are indicative of a higher frequency due to the contribution of next-nearest neighbors. The FT-EXAFS signal (Fig. 2b, dots) shows a main peak near 1.5 Å with a shoulder at 2 Å and a second peak at about 3.5 Å.

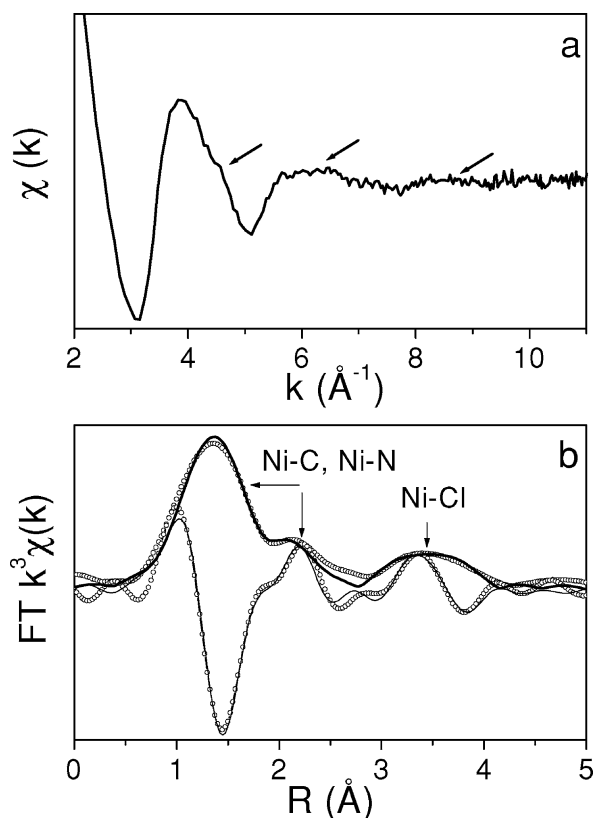


Fig. 2. (a) EXAFS signal Ni *K*-edge of in situ **1**/MAO/1-decene. The shoulders (marked by arrows) on the main oscillating contribution reflect the presence of next-nearest neighbors. (b) Modulus of the Fourier transform with the imaginary part (dots, experimental data; lines, fitted data).

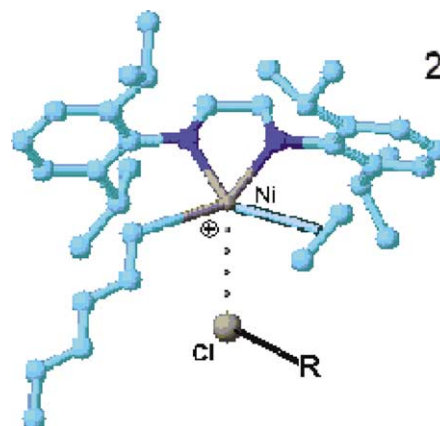
The EXAFS data were fitted considering a model with the Ni(II) atom surrounded by carbon and nitrogen atoms in the first shell and chlorine atoms at a higher distance (Fig. 2b, lines). According to the best fit, the coordination shell has the contribution of $N_C = 2.1 \pm 0.5$ carbon atoms at a distance of $R_C = 1.95 \pm 0.02$ Å and $N_N = 2.0 \pm 0.5$ nitrogen atoms at a distance of $R_N = 2.3 \pm 0.02$ Å. The mean-square relative displacements are, respectively, $\sigma_C^2 = 0.00419$ Å² and $\sigma_N^2 = 0.00965$ Å². The second peak, at about 3.5 Å, corresponds to a Ni–Cl bond with $N_{Cl} = 1.7 \pm 1$ at $R_{Cl} = 4.02 \pm 0.1$ Å and $\sigma_{Cl}^2 = 0.0176$ Å² [17].

These EXAFS data show that the active species can be best described as a complex like **2** (Scheme 1), with a nickel core containing the α -diimine ligand, the alkyl growing chain, the coordinated olefin, and a chloride atom bounded to the nickel atom in the first coordination shell. This chloride atom is probably a part of an organoaluminum moiety (R would be $Al(OR')_3$, with R' being a part of the MAO cocatalyst) [18]. The chloride atom is a part of a bridge of the type Ni–Cl–Al, in an interaction that would give a zwitterionic complex.

It can be speculated that the relatively low carbon number value that has been observed (2.1 ± 0.5) is the result of the contribution of a fraction of the nickel species with a low coordination number, and those formed by the insertion of the coordinated olefin in the nickel–carbon bond during the chain-growth process. EXAFS is not able to prove it, since it is not able to distinguish between different types of nickel–carbon bonds and can only see the average signal due to all species present in the cell.

Similar EXAFS spectra were obtained using TiBA instead of MAO, showing that very similar active species were formed with these cocatalysts.

The proposed 5-coordinated nickel intermediate explains the UV–visible data, since spin-allowed bands (high ϵ values) are expected for 5-coordinated nickel complexes [19]. This is also the case with the magnetic susceptibility data, since high-spin complexes are expected to be formed in the presence of nitrogen-bonding ligands.



Scheme 1.

The presence of the organoaluminate anion as a ligand and not as a counteranion, as previously proposed, does not change dramatically the nature of the active species. In this description, the catalyst still is an alkyl-olefin-nickel complex that is active in polymerization of olefins by sequential insertion into the nickel-alkyl bond. The model gives a better description of the active site and gives an explanation for well-known spectroscopic properties that is incompatible with the previous descriptions of these nickel(II) complexes. It can help promote understanding of the need of MAO for nickel-catalyzed α -olefin polymerization.

Nickel intermediates interacting with alkylaluminum moieties were previously proposed by Corker and Evans [5], who suggested that the interaction $\text{Ni} \cdots \text{Al}$ may be one stabilizing factor for the nickel(II) organometallics, perhaps retarding β -hydride or reductive elimination. It seems that the $\text{Ni} \cdots \text{Cl}$ interaction plays an important role, previously underestimated, in the polymerization of olefins.

Acknowledgments

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