

Study of Activation Process and Active Site of Co-Based Catalyst for 1, 3-Butadiene Polymerization Using X-Ray Absorption Spectroscopy and DFT Calculations

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ABSTRACT: Activation process and active site of Co-based Ziegler-Natta catalysts were studied by using synchrotron X-ray absorption spectroscopic technique and an optimum model of the cobalt active site was proposed with density functional theory (DFT) calculations. In the X-ray absorption near edge structure (XANES) spectrum of Co(2-ethylhexanoate)₂, the preedge peak, 1s → 3d transition at 7707.8 eV and the K-edge peak, 1s → 4p transition at 7719.2 eV were observed. Both the intense K-edge and the weak preedge peaks indicate that Co(2-ethylhexanoate)₂ possesses high O_h symmetry and the cobalt exists in a divalent state. Upon addition of methylaluminoxane (MAO), some changes in peak positions and intensities were observed. The preedge peak was a little shifted to 7708.2 eV with increased intensity, and the K-edge peak was shifted to a lower energy, 7717.2 eV with decreased intensity. This indicates that the oxidation state of cobalt still mainly remained +2 and the coordination geometry was altered from O_h to T_d resulting from Co 3d and 4p or-

bital mixing with a loss of O_h symmetry. In the XANES spectrum of a mixture of Co(2-ethylhexanoate)₂, MAO and t-BuCl, the K-edge peak at 7715.7 eV was observed. The orbital mixing of 4p cobalt and 2p chlorine orbitals results in a low energy transition. In 1,3-butadiene polymerization, this is attributable to the coordination of chlorine to cobalt, which is believed to facilitate *cis*-configuration and increasing reactivity. B(C₆F₅)₃ was employed as Lewis acid, but no significant interaction with cobalt was found in the XANES spectrum of a mixture of Co(2-ethylhexanoate)₂, Al(*i*Bu)₃, and B(C₆F₅)₃, which is similar to the XANES of a mixture of Co(2-ethylhexanoate)₂ and Al(*i*Bu)₃. B(C₆F₅)₃ as Lewis acid does not greatly disturb the coordination symmetry of cobalt nor influence the oxidation state. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2186–2190, 2009

Key words: co-based catalyst; 1, 3-Butadiene polymerization; x-ray absorption spectroscopy

INTRODUCTION

Cobalt-based catalysts for propylene oxide polymerization,¹ copolymerization of epoxides and carbon monoxide,² α -olefins and 1,3-butadiene polymerizations,^{3–6} and other reactions^{7–11} have drawn both academic and industrial interests due to their unique mechanistic pathways in comparison with early transition metals.¹² Among them, the most notable example is the cobalt-based Ziegler-Natta catalyst for 1,3-butadiene polymerization, which provides various microstructures, 1,2-vinyl, 1,4-*cis*, and 1,4-*trans*, and different polymerization activity under various catalytic conditions composed of Lewis acids and bases such as CoCl₂/pyridine/Et₂AlCl and Co(stearate)₃/MAO/*t*-butyl chloride for high *cis* polybutadiene, and CoBr₂(PPh₃)₂/Et₃Al/H₂O for syndiotactic polybutadiene.^{13–21} The nature of the active site and the functions of cocatalysts are, however,

still in dispute because it is very difficult to characterize the structure of the cobalt active-sites. Serious limitations are often met in studying the cobalt active site because of the lack of crystallinity, multi active sites, and low stability. In the present study, we employed an X-ray absorption spectroscopic technique, X-ray absorption near-edge structure (XANES), to obtain useful structural information such as oxidation state, site symmetry, and ligand structure.^{22,23}

In this article, we aim to elucidate a cobalt-based Ziegler-Natta active-site by using XANES and density functional theory (DFT) calculations. Cobalt catalyst systems, Co(2-ethylhexanoate)₂/MAO/*t*-BuCl and Co(2-ethylhexanoate)₂/Al(*i*Bu)₃/B(C₆F₅)₃, were chosen as representative models for this study.

EXPERIMENTAL

Materials

Co(2-ethylhexanoate)₂, methylaluminoxane (MAO, 10 wt % in toluene), triisobutylaluminum (1.0M in

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hexanes), *t*-BuCl and $B(C_6F_5)_3$ were purchased from Aldrich.

Cobalt catalyst preparation

The active Ziegler-Natta catalysts for XAS experiments, were prepared under nitrogen at room temperature: (1) $Co(2\text{-ethylhexanoate})_2$ (1.0 ml, 1.0M in cyclohexane), MAO (15 ml, 10% toluene), and *t*-BuCl (15 ml, 1.0M in cyclohexane) were added in order. The ratio of Co, Al, and Cl in cobalt catalyst was $Co/Al/Cl = 1/22/15$ at Co conc. of 1.0×10^{-3} mol; (2) $Co(2\text{-ethylhexanoate})_2$ (1.0 ml, 1.0M in cyclohexane), $Al(iBu)_3$ (6 ml, 1.0 M hexanes), and $B(C_6F_5)_3$ (15 ml, 0.33 M in toluene) were added in order. The ratio of Co, Al, and Cl in cobalt catalyst was $Co/Al/B = 1/60/50$ at Co conc. of 1.0×10^{-3} mol.

XAS measurement and data analysis

The cobalt samples were placed in an air-tight X-ray absorption spectroscopy (XAS) cell made of Teflon with two Mylar windows (1/2000 inch; window size, 20×8 mm; optical path length, 2 mm). Co K-edge XAS measurement was carried out using Beam Line 3-C (2.0 GeV; 80–150 mA; Si(111) double flat crystal monochromator) at the Pohang Accelerator Laboratory (PAL) at POSTECH, Korea. XAS data were collected at room temperature in the transmission mode using ion chamber detectors filled with N_2/Ar mixture. The monochromator was detuned by 20% in incident X-ray beam. All data were internally calibrated using Co foil (K-edge, 7709 eV). The near-edge region was scanned at equal energy step of 0.30 eV/point to resolve fine structures. The primary data, $\ln(I_0/I_t)$, were normalized after extending the preedge region to the postedge region using the Victoreen formula. The transition energies were obtained by taking the first-derivative spectra.

Calculations

Geometry optimizations were carried out without any symmetry constraints, using the density functional theory at the generalized gradient approximation level, BLYP functional.^{24,25} Double numerical plus polarization basis sets were used for all atoms. All calculations were performed using the DMOL3 program,^{26,27} as available in Accelrys' Material Studio suite of programs.

1,3-Butadiene polymerization

(1) Cyclohexane (500 g), 1,3-butadiene (100 g), $Co(2\text{-ethylhexanoate})_2$ (1.0 ml, 0.1M cyclohexane), MAO (1.5 ml, 10% toluene) and *tert*-butyl chloride (1.0M *n*-heptane) were added to a 2-L pressure reactor under

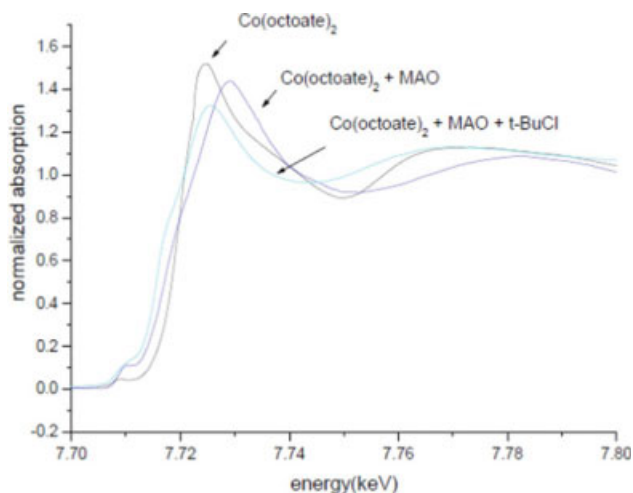


Figure 1 Co-XANES spectra of the activation of $Co(2\text{-ethylhexanoate})_2$ with MAO and *t*-BuCl. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

a nitrogen atmosphere, and reacted at 60°C for 2 h. The resulting polybutadiene was stabilized with 2,6-di-*tert*-butyl-4-methylphenol (0.5 g), and terminated by methanol. (2) Cyclohexane (500 g), 1,3-butadiene (100 g), $Co(2\text{-ethylhexanoate})_2$ (1.0 ml, 0.1M cyclohexane), $B(C_6F_5)_3$ (1.5 ml, 0.33M in toluene), and triisobutyl aluminum (0.6 ml, 1.0 M *n*-heptane) were added to a 2-L pressure reactor under a nitrogen atmosphere, and reacted at 60°C for 2 h. The resulting polybutadiene was stabilized with 2,6-di-*tert*-butyl-4-methylphenol (0.5 g), and terminated by methanol.

RESULTS AND DISCUSSION

Co K-Edge XAS measurement

Normalized Co K-edge XANES spectra of $Co(2\text{-ethylhexanoate})_2$ and cobalt species formed during activation steps are shown in Figure 1 and summarized in Table I. The intense K-edge absorption peak of cobalt, which depends on the geometrical symmetry, provides structural information such as the oxidation state and symmetry.^{22,23} The preedge peak, due to dipole-forbidden but quadruple-allowed transition of $1s \rightarrow 3d$, is also an indication of site symmetry around cobalt (II). In the X-ray absorption near edge structure (XANES) spectrum of $Co(2\text{-ethylhexanoate})_2$, the preedge peak, $1s \rightarrow 3d$ transition at 7707.8 eV, and the K-edge peak, $1s \rightarrow 4p$ transition at 7719.2 eV, were observed. The weak preedge peak of $Co(2\text{-ethylhexanoate})_2$ implies that cobalt ($t_{2g}^6 e_g^1$) with T_{1u} symmetry is surrounded by a highly symmetrical octahedron of six oxygen atoms, resulting in minimal orbital hybridization of 3d and 2p orbitals.^{28–30}

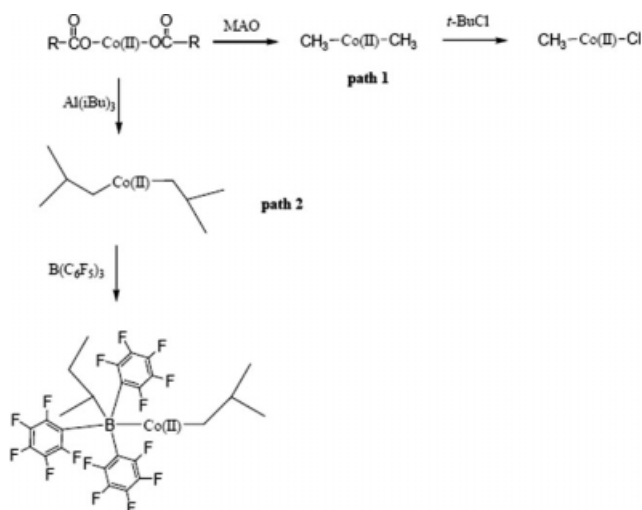
TABLE I
Preedge and K-Edge Peak Positions of the Activated species of Co(2-ethylhexanoate)₂/MAO/*t*-BuCl and Co(2-ethylhexanoate)₂/Al(*i*Bu)₃/B(C₆F₅)₃

Cobalt species	Transition	Energy (eV)
Co(octooate) ₂	1s → 3d	7707.8
	1s → 4p	7719.2
Co(octooate) ₂ + MAO	1s → 3d	7708.2
	1s → 4p	7717.2
Co(octooate) ₂ + MAO + <i>t</i> -BuCl	1s → 3d	7708.2
	1s → 4p	7715.7
Co(octooate) ₂ + Al(<i>i</i> Bu) ₃	1s → 3d	7708.6
	1s → 4p	7716.7
Co(octooate) ₂ + Al(<i>i</i> Bu) ₃ + B(C ₆ F ₅) ₃	1s → 3d	7708.6
	1s → 4p	7715.3

octooate = 2-ethylhexanoate.

Co(2-ethylhexanoate)₂/MAO/*t*-BuCl active species

A Ziegler-Natta cobalt catalyst, Co(2-ethylhexanoate)₂/MAO/*t*-BuCl, was employed for a structural study of a cobalt catalytic system during activation, Scheme 1. A large change was observed in Co(2-ethylhexanoate)₂ where methylaluminoxane (MAO) alone as alkylating catalyst was used to form Co—C bond and to initiate polymerization. The preedge peak with increased intensity remained at 7708.2 eV but the K-edge peak with decreased intensity shifts to a lower energy position, 7717.2 eV from 7719.2 eV. While peak positions tell that the oxidation state of cobalt mainly remained +2. A large reduction of the main absorption (K-edge) peak and a relative enhancement of the preedge peak indicate that the symmetry changed from O_h to T_d structure. Lowered symmetry is a strong indication of increased orbital mixing between the 3d and 4p cobalt orbitals, and overlap of the cobalt 3d orbitals with the ligand



Scheme 1 Catalyst activation paths of the cobalt-based Ziegler-Natta Catalysts for 1,3-butadiene polymerization.

2p orbitals. Since a new coordination site for 1,3-butadiene should be available for polymerization to take place, the coordination geometry around cobalt is to be altered from a highly saturated O_h geometry. As chlorine was added, the K-edge peak was shifted to a low energy at 7715.7 eV. The shift is attributed to a strong interaction between chlorine and cobalt. This is an evidence that indicate chlorine works as one of main ingredients in active species during 1,3-butadiene polymerization, in which activity (1.7 × 10⁵ g/ Co mol·h) greatly increases with high *cis* configuration (95.5%).

Co(2-ethylhexanoate)₂/Al(*i*Bu)₃/B(C₆F₅)₃ active species

The other Ziegler-Natta cobalt catalyst, Co(2-ethylhexanoate)₂/Al(*i*Bu)₃/B(C₆F₅)₃, was employed for a structural study of a cobalt catalytic system during activation, Scheme 1. In the XANES spectrum of a mixture of cobalt 2-ethylhexanoate and Al(*i*Bu)₃, K-edge peak was shifted to 7716.7 eV from 7719.2 eV in Figure 2. The oxidation state was mainly +2. B(C₆F₅)₃ was employed to activate polymerization with high *cis* configuration and to stabilize the active site. No appreciable shape-change in the preedge and K-edge of the XANES spectrum of Co(2-ethylhexanoate)₂/Al(*i*Bu)₃/B(C₆F₅)₃ was observed in comparison with that of Co(2-ethylhexanoate)₂ and Al(*i*Bu)₃. This result indicates that B(C₆F₅)₃ did not make any significant covalent bonding with cobalt. However, under only a catalyst composed of Co(2-ethylhexanoate)₂ and Al(*i*Bu)₃ without B(C₆F₅)₃ in cyclohexane, any conversion or high *cis* configuration was not obtained. During 1,3-butadiene polymerization, B(C₆F₅)₃ is believed to be involved in the

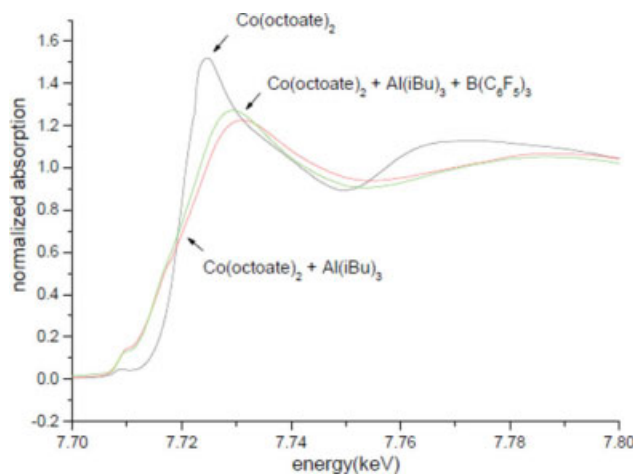


Figure 2 XANES spectra of the activation of Co(2-ethylhexanoate)₂ with Al(*i*Bu)₃ and B(C₆F₅)₃. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

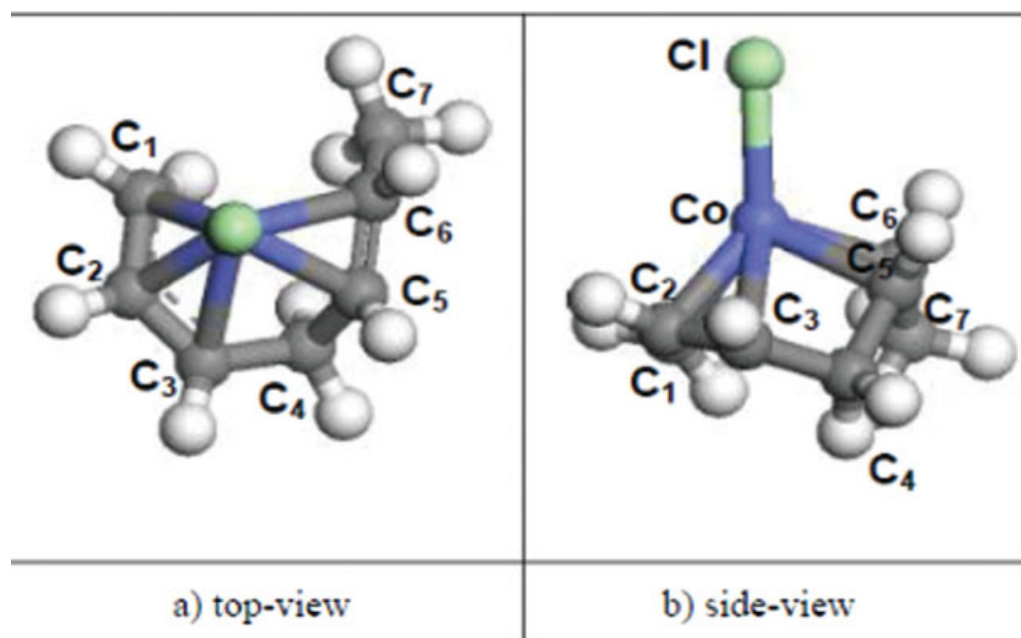
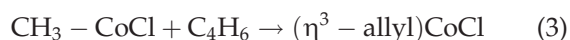
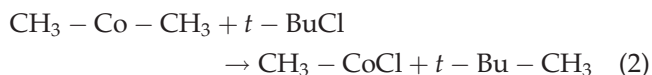
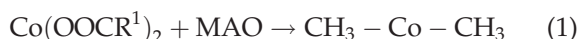


Figure 3 Model of an active site of the cobalt-based Ziegler-Natta catalyst for 1,3-butadiene polymerization (Co—C₁ 2.120 Å, Co—C₂ 2.088 Å, Co—C₃ 2.365 Å, Co—C₅ 2.105 Å, Co—C₆ 2.093 Å, C₅—C₆ 1.408 Å, Co—Cl 2.297 Å, C₁—C₂ 1.433 Å, C₂—C₃ 1.402 Å, C₅—C₆ 1.408 Å). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

active center, and its Lewis acidity increases *cis* content and activity. Non-directing interaction of B(C₆F₅)₃ on cobalt results in a relatively low activity, 4.7×10^4 g/Co mol · h, in comparison with the active site composed of chlorine, and yields a *cis* content, 71.7%.

Active-Site structure and mechanism

The cobalt active-site, composed of Co(2-ethylhexanoate)₂, MAO and *t*-BuCl, is proposed with XANES data and density functional calculations.^{24,25} As below in eqs. (1)–(3), Co-catalyst is activated.



The highly active site is formed by alkylation [eq. (1)] and by ligand exchange reaction with chloride [eq. (2)]. The optimized structure shows that the allyl chain end, chloride, the penultimate double bond are coordinated to Co(II), and the symmetry is tetrahedral in Figure 3. The bond distances are Co—C₁ 2.120 Å, Co—C₂ 2.088 Å, Co—C₃ 2.365 Å, Co—C₅ 2.105 Å, Co—C₆ 2.093 Å, Co—Cl 2.297 Å, C₁—C₂ 1.433 Å, C₂—C₃ 1.402 Å, and C₅—C₆ 1.408 Å, respectively. The penultimate double bond

(C₅, C₆) surrounds cobalt center, and the bond length of Co—C₁ is shorter than that of Co—C₃. The *cis* or *trans* configuration favored over vinyl one is attributable to the allylic end like η^1 -coordination in

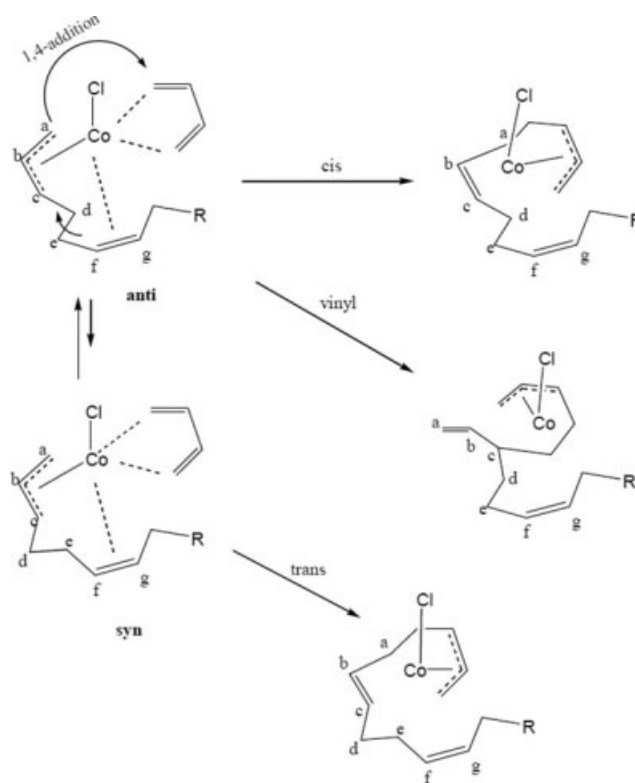


Figure 4 Proposed mechanism of 1,3-butadiene insertion on cobalt active-site.

Figure 4. The function of chlorine directing high *cis* stereoregularity is proposed by the inductive effect of chlorine over 3d-orbitals of cobalt so as to facilitate the back-biting coordination of the penultimate double bond that hinders *anti-syn* isomerization. Trans effect of chloride is a good model to explain the insertion mechanism of 1,3-butadiene, in which incoming butadiene competes with the penultimate double bond for a coordination site on cobalt.

CONCLUSIONS

Through this work we understand the nature of the cobalt active-site and the functions of cocatalyst for 1,3-butadiene polymerization for high *cis* configuration using synchrotron X-ray absorption and DFT calculations, the following conclusions are reached: (1) the active cobalt mostly remains in a divalent state, and the geometrical change from O_h to T_d structure around cobalt occurs with the addition of alkyl aluminum, (2) Co(II) is the center of the active site composed of Co(II)- η^1 -allyl and Co(II)-penultimate bonds, (3) Co(II)- η^1 -allyl facilitates *cis* or *trans* configuration, and Co(II)-penultimate bond promotes high *cis* configuration in an *anti* conformation, (4) chlorine works as one of main ingredients in active species during 1,3-butadiene polymerization, in which activity greatly increases with high *cis* configuration, (5) $B(C_6F_5)_3$ as Lewis acid does not greatly disturb the coordination symmetry of cobalt, but leads polymerization activity with high *cis* configuration.

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