First in-Situ Observation of Pseudoliving Character and Active Site of Nd-Based Catalyst for 1,3-Butadiene Polymerization Using Synchrotron X-ray Absorption and UV−Visible Spectroscopies

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Introduction. The importance of living polymerization and high stereoregularity in industry has developed lanthanide-based catalysts.[1] Among Ziegler−Natta catalysts currently being used in the rubber industry for the high cis 1,4-polymerization of 1,3-butadiene, the Nd-based catalyst (Nd(carboxylate)$_3$/AlEt$_2$Cl/Al(^{i}Bu)$_3$) is of particular interest because it gives a cis microstructure (up to 99%) higher than any other catalysts and has pseudoliving character that is very rare in Ziegler−Natta catalysts.[2−4] In the course of understanding the pseudoliving character and the active site around neodymium, in-situ spectroscopic observation on the active site was conducted using synchrotron X-ray absorption and UV−vis spectroscopies.

Results and Discussion. Under a N_2 atmosphere the active neodymium-based catalyst was prepared by mixing neodymium neodecanoate (ND, 0.10 mmol, 11.8% Nd in *n*-heptane), Al(^{i}Bu)$_3$ (4.00 mmol, 1.0 M *n*-heptane), and AlEt$_2$Cl (0.30 mmol, 1.0 M *n*-heptane) in order at room temperature. The neodymium at each activation step was rapidly frozen at −78 °C and then placed in an airtight X-ray absorption spectroscopy (XAS) cell made of Teflon with two Mylar windows (1/2000 in.; window size, 20 mm × 8 mm; optical path length, 2 mm) (Figure 1). In the transmission mode, synchrotron XAS monitored the coordination sphere and the oxidation state of neodymium and provides vital structural information: XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure). The evolvement of normalized XANES spectra of Nd L_{III} absorption edges at each activation step is shown in Figure 2. The absorption edges arise from electronic transition from core $2p_{3/2}$ level to vacant 5d states of neodymium atom and are named the "white line (WL)".[5] The position of the white line of ND (Nd(neodecanoate)$_3$) was observed at 6216.0 eV, which is the same position as the WL of $Nd_2(III)O_3$ powder having ionic character appearing at 6216.1 eV. The WL position and high intensity of ND indicate that the Nd is in the trivalent state and has strong ionic character.[6] A little downshift of WL of NDA was observed at 6214.8 eV where a large excess of alkylaluminum (40 Al/Nd mol ratio) was employed. The same shift was also observed at the XANES of NDAC. Even upon addition

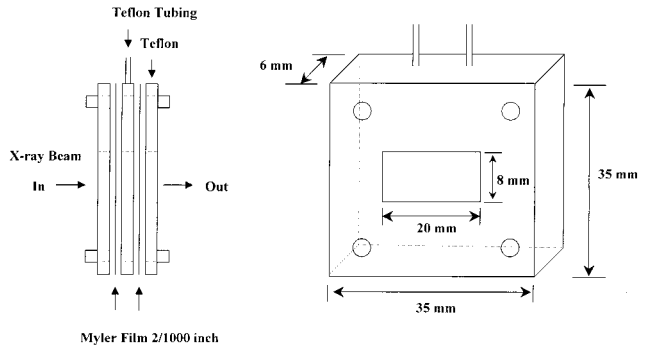

Figure 1. XAS cell for liquid and air-sensitive catalyst.

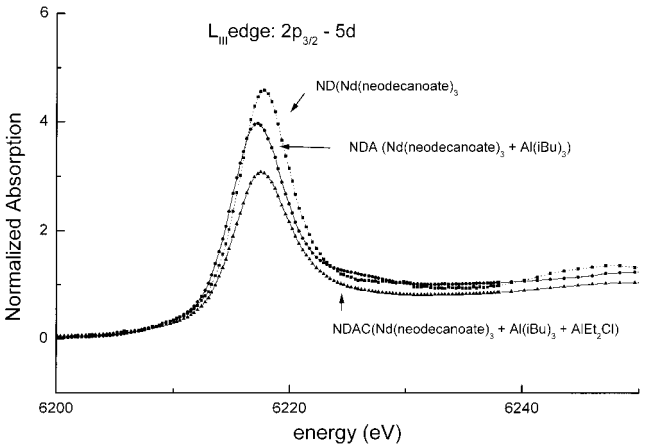

Figure 2. Nd-L_{III} edge XANES spectra of ND, NDA, and NDAC.

of a large amount alkylaluminum and alkylaluminum chloride, Nd remains in the same oxidation state which implies the high oxidation stability of neodymium(III). This result is remarkably different than the Ni- or Ti-based Ziegler−Natta catalyst. In the nickel catalyst composed of Ni(naphthenate)$_2$ and AlEt$_3$, rapid reduction of nickel(II) to nickel(0) takes place as alkylaluminum is added.[7] A little downshift of WLs of NDA and NDAC reflects formation of Nd−C bond having partly covalent character, and the decreased WLs indicate the more disordered coordination sphere of neodymium.[8] The spectral low sensitivity even in the ligand change during the activation steps arises from lack of π-back-bonding to carbon due to empty d-orbitals and supports that neodymium holds the high polarity. In this respect the chain end Nd−C bond in 1,3-butadiene polymerization is so polar that pseudoliving polymerization of conjugated dienes with neodymium catalyst is possible, which is very difficult with a transition metal catalyst such as Ti, Co, or Ni.[2]

Figure 3 is phase-uncorrected Fourier transformed (FT) spectra of k^3-weighted EXAFS. The pronounced peak of ND located at 1.85 Å arises from the scattering of the oxygen atoms located at the first coordination sphere, and the broad peak indicates Nd(neodecanoate)$_3$ does not have well-ordered structure. Compared with the XANES spectra, considerable changes of the peaks in position and shape were observed in the FT spectra of NDA and NDAC. The main peak of NDA located at 1.38 Å and the decreased magnitude are attributed to forming Nd^{3+}−C in place of the Nd^{3+}−O bond in the

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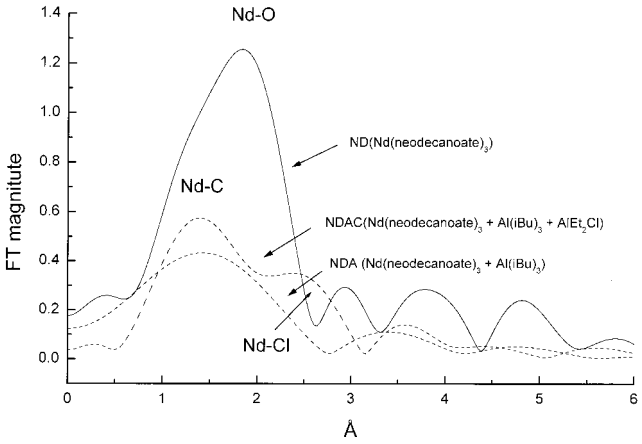

Figure 3. Fourier transforms of EXAFS spectra of ND, NDA, and NDAC (k range of 2−11 Å^{-1}).

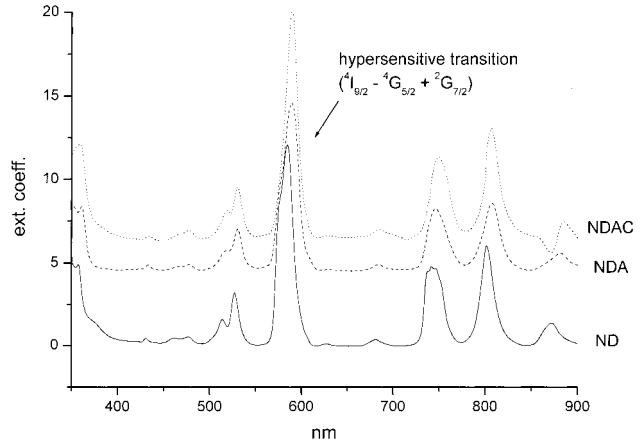

Figure 4. UV−vis absorption spectra of ND, NDA, and NDAC.

first coordination sphere by addition of Al(^{i}Bu)$_3$. In the FT spectrum of NVDC, the two main peaks appear, and the first located at 1.41 Å and the second located at 2.49 Å are partly overlapped. The first peak is located at a position similar to that of NDA and hence attributed to the Nd−C bond. The second peak is attributed to the Nd^{3+}−Cl peak formed by the addition of AlEt$_2$Cl, which promotes high cis formation during 1,3-butadiene polymerization.[2d−f]

The ionic character of neodymium was also observed in the in situ UV−vis spectroscopic measurement carried out on each activation step by the sequent addition of neodymium neodecanoate, Al(^{i}Bu)$_3$, and AlEt$_2$Cl like the XAS measurement. Sharp absorption peaks at 527, 584, 741, and 801 nm, f−f electronic transitions of neodymium by spin−orbit coupling between 4f^n configurations,[9] were observed at the almost same positions in the all spectra of ND, NDA, and NDAC (Figure 4). The little spectral change, the small spectral bandwidth, and the low intensity of the absorption ($\epsilon_{max} \approx 10$ at 584 nm) all represent strong ionic character of neodymium having little involvement in bonding with the ligand orbital. A slight red shift was observed upon addition of Al(^{i}Bu)$_3$ and AlEt$_2$Cl to neodymium neodecanoate, which apparently results from nephelauxetic effect by the combination of the orbitals of Nd−C bond forming partly covalent bond. It is also notable that the shoulder of the hypersensitive transition at 584 nm, attributed to $^4I_{9/2} \rightarrow {}^4G_{5/2} + {}^2G_{7/2}$ and particularly sensitive to changes in the coordination sphere, disappeared in the spectra of NDA and NDAC.[10]

Conclusion. We have demonstrated how synchrotron X-ray absorption and UV−vis spectroscopies could be applied in situ to study structural and electronic aspects of a homogeneous catalyst. In combination with XANES, EXAFS, and UV−vis spectroscopic data on the neodymium-based catalyst, the following are concluded: (1) The pseudoliving property of the neodymium-based catalyst originates from the contact Nd^{3+}−C bond having both covalent and ionic character, of which the bond length is 1.41 Å as a phase-uncorrected value. (2) Neodymium keeps the trivalent state during the activation process. (3) Nd(neodecanoate)$_3$ does not have a well-ordered structure, and the bond length of Nd−O is 1.85 Å. (4) The Nd−Cl bond forms in the long length of 2.49 Å.

Experimental Section. a. XAS Measurement and Data Analysis. Nd L$_{III}$-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 N_2 (I_0) and Ar (I) filled ionization detectors. The monochromator was detuned by 20% in incident X-ray beam. All data were internally calibrated using Mn foil (K-edge, 6539 eV). The near-edge region was scanned at equal energy step of 0.30 eV/point to resolve fine structures. The EXAFS spectra were obtained at constant wave vector k, 0.05 Å^{-1}. The primary XAS data, $\ln(I_0/I_t)$, were normalized after extending the preedge region to the postedge region using the Victoreen formula. EXAFS was extracted from the normalized XAS spectra after converting from electronvolts to wave vector (k) by the equation $k = [0.263(E - E_0)]^{1/2}$ and fitting with a routine (AUTOBK) provided in the UWXAFS package (version 3.0). The EXAFS, $\chi(k)$, is described by the following equation:

$$\chi(k) = \sum_R N_R S_0{}^2 \frac{f_{\text{eff}}}{kR^2} \sin(2kR + \phi(k)) \exp(-2k^2\sigma^2) \times \exp(-2R/\lambda)$$

The parameter of our primary interest is the interatomic distance, R. We multiplied $\chi(k)$ by k^3 to enhance the oscillatory part at high k.

b. UV−Visible Spectroscopy Measurement. The electronic spectra were obtained in an airtight quartz cell with a JASCO V-570 UV/vis/near-IR spectrophotometer at room temperature.

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