



Origin of broad molecular weight distribution of polyethylene produced by Phillips-type silica-supported chromium catalyst

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ABSTRACT

The origin of the broad molecular weight distribution of polyethylene produced by Phillips-type silica-supported chromium (Cr/SiO_2) catalysts was studied by density functional calculations using active site models with various coordination environments. Difference of the coordination environment of chromium showed remarkable variations for both of the insertion and the chain transfer energies, resulting in a broad range of molecular weight from 10^2 to 10^{10} g/mol at 350 K. The results clarified that the special catalytic property of Cr/SiO_2 for broad molecular weight distribution is attributed to the heterogeneity of the coordination environment of the chromium species.

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1. Introduction

Phillips catalysts [1] composed of CrO_x supported on SiO_2 (Cr/SiO_2) have long maintained their industrial importance after the discovery in 1950s in the polyolefin manufacture to produce nearly 7 million tons of a special grade of high density polyethylene (HDPE) per year over the world. The specialty of the Cr/SiO_2 catalysts is an ability to produce HDPE with fine mechanical properties such as elasticity and impact resistance, and with superior moldability due to its high melt viscosity. They come from both broad molecular weight distribution (MWD) and adequate amounts of short and long chain branches, which are automatically produced in ethylene homopolymerization [2]. As finer controls of polymer structures with the Cr/SiO_2 catalysts have been continuous demands for further multi-purpose materials, significant efforts still deposit obscurities in the mechanistic origin of the unique catalytic features.

The broad MWD has been believed to be mainly of a chemical origin, while some physical influences such as monomer concentration gradients within catalyst particles were also reported [3]. The chemical origin has been regarded as the heterogeneity of supported Cr species. Specifically, the conventional catalyst synthesized by an impregnation method makes a mixture of several types of potentially active Cr(VI) species and inactive Cr_2O_3 clusters [4–9]. In past years, many researchers have tried to investigate structures of Cr(VI) species. Applying UV–vis diffuse reflectance, Raman

and X-ray adsorption spectroscopies (XAS), Weckhuysen et al. [10] found mono- and dichromate with tetrahedral symmetry mainly present on the surface. Dichromate species are dominant among Cr(VI) at high Cr loadings and/or high calcination temperatures. However, since surface structures can be sensitive to the surface chemistry of oxide supports, the nuclearity of Cr(VI) is still under debate [11]. Furthermore, reduced Cr species, which are transient states between Cr(VI) and lower valence active species, exhibit a variation in the bonding and the interaction with surface oxygen. Such heterogeneity of coordination environment around Cr leads to a variety of symmetry and oxidation states of reduced Cr species. For example, UV–vis spectroscopy and XAS showed the presence of pseudo tetrahedral Cr(II), pseudo octahedral Cr(II) and pseudo octahedral Cr(III) on a reduced catalyst [12,13]. A recent report by Gianolio et al. [14] showed a direct evidence of the coordination of surface siloxane ligands to reduced Cr species by the EXAFS, which is believed to be crucial for giving a variety of coordination environments around reduced Cr species. In an IR study by Zecchina et al. [15–17], three types of reduced species were identified (named as species A, B and C) through the adsorption of CO. Thus, Cr species on SiO_2 can be roughly classified in terms of two kinds of heterogeneities: (1) nuclearity and (2) coordination environment.

Several Phillips-type model catalysts with uniform Cr structures have been designed in order to reduce the above-mentioned heterogeneity. For example, Amor Nait Ajjou and Scott [18–20] supported dialkylated Cr(IV) mononuclear species on SiO_2 by chemical vapor deposition (CVD) of CrNp_4 ($\text{Np} = \text{Neopentyl}$). Ikeda and Monoi reported a model catalyst with monoalkylated Cr(III) mononuclear species supported on SiO_2 , using a molecular precursor of $\text{Cr}(\text{CH}(\text{SiMe}_3)_2)_3$ [21]. Both of the model catalysts showed quite

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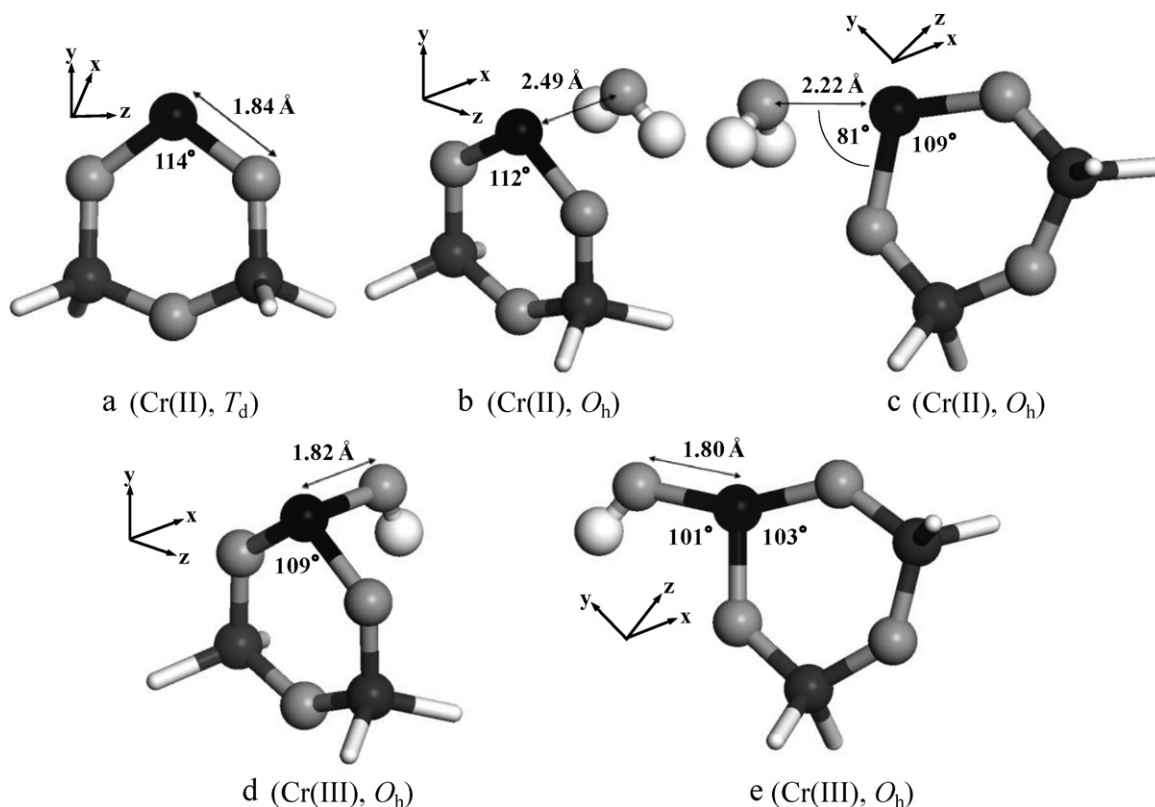


Fig. 1. Active site models with various coordination environments. Black: Cr, dark gray: Si, gray: O, white: H.

high activity for ethylene polymerization, and the MWDs of produced HDPEs were surprisingly very broad comparable with that obtained from impregnated catalysts, in spite of the almost uniform Cr nuclearity and oxidation state. It is believed that the heterogeneity of Cr species exists for these model catalysts due to the difference of the coordination environment around Cr species. On the other hand, Nenu et al. reported that an impregnated Cr/SiO₂ catalyst behaved like a single-site catalyst, giving very narrow MWD close to 2, when 1,3,5-tribenzylhexahydro-1,3,5-triazine was added as a coordinative ligand to Cr species [13,22,23]. Obviously, all these results suggest much larger contribution of the coordination environment of Cr to broaden MWD than that of the nuclearity.

In this contribution, we present the first molecular-level investigation for influences of coordination environments of Cr on the MW of PE. The apparent free energies of activation for the ethylene insertion to growing chain and chain transfer (CT) to coordinated ethylene were calculated by density functional theoretical (DFT) calculation for various active site models. The results obtained here have disclosed active site structures of Cr for broadening MWD of PE, and have provided valuable insights in the catalytic properties of Cr/SiO₂ catalysts as well as in molecular chemistry of these elemental reactions. To the best of our knowledge, DFT investigation on the origin of unique structures of produced PE by Phillips catalysts has never been undertaken so far.

2. Numerical details

All the DFT results were obtained using DMol3 as implemented in the Materials Studio (Version 4.2) [24]. The exchange–correlation functional of Perdew–Burke–Ernzerhof [25] (PBE), which is one of the most frequently used functional on the study of catalytic reactions on heterogeneous metal oxide catalysts, was employed. The basis set was the double numeric with d-polarization functions

except for hydrogen (DND) combined with effective core potentials (ECP) [26,27]. The real space cutoff radius was 4.400 Å. The convergence criterion for SCF calculations was 1.0×10^{-5} Hartree, and those for geometry optimization were 2.0×10^{-5} Hartree for energy and 4.0×10^{-3} Hartree/Å for the maximum force. A high-spin state was always favored for Cr(IV), Cr(III) and Cr(II). Transition states (TS) of both ethylene insertion and CT reaction were obtained by TS optimization based on the Newton–Raphson algorithm. The CT reaction in ethylene polymerization with Cr/SiO₂ catalysts is known to mainly occur through β -hydrogen transfer to ethylene [28].

The size of the employed basis set was rather small in obtaining converged energies. Especially, the lack of diffuse functions on Cr leads to underestimation of the energies of π -complexes and TSs compared with the energy of gas-phase ethylene and a monomer-free active site, resulting in overestimation of π -complexation energies and underestimation of activation energies. However, as described later, the present task is to estimate the energetic difference between two activation energies (see Eq. (3)) rather than quantitative evaluation of the above values. Considering the cancellation of errors for differential values, the employed basis set could fulfill our target to compare MWs among various coordination environments. Actually the magnitude of MW estimated for the most basic active site (Fig. 1, model a) was the same when a larger basis set (DNP) and higher convergence criteria (fine) were employed.

To elucidate effects of coordination environments on the MW of PE, five cluster models a–e were employed in Fig. 1. Cr was basically supported on the minimum –O–Si(H₂)–O–Si(H₂)–O– framework, although the effects of the chromasiloxane ring size and those of the hydrogen termination were also investigated. Such 6-membered chromasiloxane ring was regarded as one of the most plausible species by Espelid and Børve [29], and Demmelmaier et al. reported

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