Activity of phenoxy-imine titanium catalysts in ethylene polymerization: A quantum chemical approach

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ABSTRACT

The mechanism of ethylene polymerization on phenoxy-imine (FI) titanium catalysts was studied theoretically to identify the major factors affecting the catalytic activity. Geometry optimizations of FI ligands, octahedral titanium dichloride complexes, active cationic species, and their π-complexes with ethylene as well as calculations of the energy profile of chain propagation were performed at the BP86-D3 level. We found that the calculated energy gaps between frontier orbitals (HOMO and LUMO) in the active cations of the catalysts correlate with the experimental activity values. High activities of FI catalysts with α-Cumyl groups were attributed to smaller HOMO-LUMO gaps due to hyperconjugation between π-systems of α-Cumyl and (N-aryl)salicylaldimine moieties in the active cations. The correlation provides a qualitative estimate of the catalytic activity for further design of new FI titanium complexes.

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1. Introduction

Novel polyolefinic materials, e.g. ultra-high-molecular-weight polyethylene (UHMWPE), attract the attention of both scientists and engineers due to many useful properties, namely, light weight, excellent mechanical strength, chemical inertness, flexibility, resistance to abrasion, and recyclability. Moreover, UHMWPE is an inexpensive and commercially available substance. These features make it a competitive raw material for manufacture of various valuable products, such as ship ropes, biological prostheses, bullet-proof vests and helmets, protective gloves, car bumpers, and artificial ice [1,2].

Nowadays UHMWPE is mostly prepared by coordination polymerization of ethylene on three main types of catalysts: Ziegler-Natta, metallocene, and post-metallocene [3]. Homogeneous single-site catalytic systems based on phenoxy-imine (FI) titanium dichloride complexes of the post-metallocene type with methylalumoxane (MAO) as a cocatalyst were reported to show high activity in olefin polymerization [4]. The chemical structure of such complexes facilitates the synthesis of a large variety of cat-

alysts, that in turn allows for preparation of UHMWPE of various molecular weight distribution, structure, and morphology [3,5].

Recent studies by Ivanchev et al. [6–10] revealed that FI titanium catalysts bearing a double bond in the ligand structure are capable of self-immobilization during ethylene polymerization. This process results in special morphological features of the resulting PE and thereby makes the product recyclable by a cold gel-formation procedure [11]. Furthermore, Fujita et al. [12–15] demonstrated that the use of FI catalysts with ortho-fluorinated N-aryl groups allows to perform olefin polymerization in controlled "living" mode and thus to synthesize polymers of various well-defined architectures. Such modifications in the structure of a FI ligand primarily affect catalytic activity and molecular weight distribution of the resulting polymer [3]. In many cases nontrivial organic syntheses of the catalysts as well as numerous polymerization experiments and characterization assays of final polymers are required to find out how these parameters vary for different complexes. Thus, a simple method for estimation of activity and molecular weight distribution without any chemical experiments would be a powerful tool for design of new active FI catalysts.

Many studies have been conducted on correlations between experimental values of catalytic activities in ethylene polymerization and theoretical quantum chemical parameters. Remarkable results in this field have been obtained by Cruz and co-workers [16–20] who applied the 3D-QSAR approach to research into single-site polymerization catalysts of both the metallocene and the

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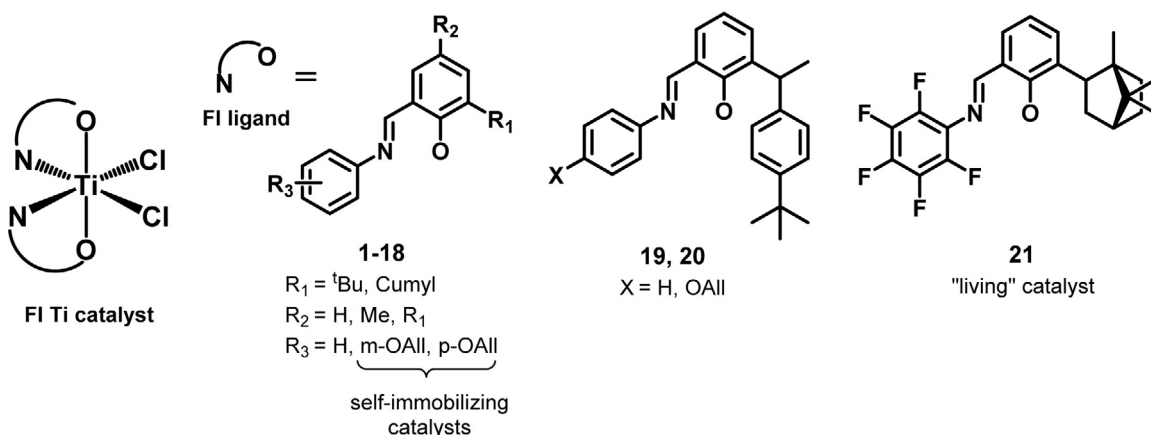
Fig. 1. Chemical structures of FI titanium catalysts studied in this work.

post-metallocene type. The authors established relations for quantitative evaluation of both catalytic activity and polymer molecular weight with a high degree of accuracy. The strong predictive power of the proposed method can be associated with thorough consideration of structural aspects in both steric and electronic effects of a ligand.

In recent studies, Sun et al. [21–24] demonstrated that activity values for post-metallocene catalysts with late transition metals can be quantitatively predicted using hybrid DFT-QEq calculations. In these works, apart from initial complexes, correlations were determined for active species formed during the polymerization process. These results are of special interest since it is well-known that the initial form of a post-metallocene catalyst by itself cannot perform ethylene polymerization, and the structure of the active species in general differs considerably from that of the pre-catalyst.

Within the framework of the "ligand-oriented concept," Fujita et al. [25] found correlation between experimental activity of FI catalysts and electronic flexibility of the ligand which in turn was determined by the energies of frontier orbitals (HOMO and LUMO) in the ligand structure calculated at the MNDO-PM3 level. Employing MM-QEq calculations, HuaYi and co-workers [26] evaluated the influence of the metal net charge in a large number of FI titanium and zirconium dichloride complexes. Although structure-activity relations in these studies had more qualitative nature, both research groups came to the conclusion that electron-withdrawing groups in the ligand of a complex are favorable for high activity in ethylene polymerization under mild conditions.

In the present work, we theoretically analyze the mechanism of ethylene polymerization on FI titanium dichloride complexes and establish correlations for qualitative estimation of the catalytic activity values by means of DFT calculations of active cationic species and related structures.

2. Computational methods

All computations were performed using the ORCA 3.0.3 software package [27] on a parallel platform of the LUNARC center for high-performance computing [21]. Optimal parameters for the calculations (the DFT functional and the basis set) were chosen after a comparison of optimized geometries of dichloride complexes with the corresponding experimental X-ray structures (see Supporting information). The geometry optimizations were performed with BP86 exchange-correlation functional and SVP split-valence basis set for all atoms [28–30]. In the case of energy barrier calculations, the D3BJ atom-pairwise dispersion correction with Becke-Johnson damping was added to the functional, and the basis set was extended to TZVP. In order to confirm the type of stationary

points (minima or transition states), eigenvalues of the numerical hessian were computed. For assessment of the solvent effect in the energy barrier calculations (for single point energies) we utilizied the COSMO continuum solvation model [31]. Natural population analysis was performed in the JANPA 1.02 software [32].

3. Results and discussion

3.1. The calculated structures of FI titanium catalysts

For our computations we selected a series of FI titanium catalysts **1–21** that were previously used for ethylene polymerization by Ivanchev and Fujita and co-workers (Fig. 1) [6–10,33–36].

The series includes two complete sets containing nine dichloride complexes with α-^{t}Bu and α-Cumyl [2-(2-phenylpropyl)] substituents in the ligand structure (**1–18**). Each set includes six self-immobilizing catalysts with an allyloxy group (OAll) in the N-aryl moiety. Such sets were chosen to find a theoretical explanation of the higher catalytic activities of FI titanium and zirconium dichloride complexes bearing α-Cumyl substituents as compared to their α-^{t}Bu analogs. This phenomenon was previously attributed to higher steric bulkiness of α-Cumyl(s) as compared with α-^{t}Bu(s) [37,40]. Here, we show that the electronic structure of an α-Cumyl group is also responsible for high activities of the corresponding catalysts. In order to evaluate the impact of the steric effect and the "living" character of the polymerization on the activity, we also analyzed two FI titanium catalysts with α-1-(4-(tert-butyl)phenyl)ethyl substituents (**19, 20**) and one with ortho-fluorinated N-aryl groups (**21**). Note that, since the accurate structure-activity relation was not the aim of this work, we used activity values that were measured under close but not exactly the same experimental conditions (see Supporting information). For some catalysts, due to the lack of the necessary experimental data, the activities were estimated from two closest temperature points. It is well-known that catalytic activity is strongly affected by polymerization conditions. Nonetheless, we believe that for qualitative relations between experimental and theoretical data, which are the aim of this work, the accuracy of the estimated values is acceptable.

3.2. Analysis of the polymerization mechanism

The time-averaged activity of FI titanium catalysts **1–21** in ethylene polymerization measured by Ivanchev [6–10,34] and Fujita et al. [3,12–15,25,37–40] is defined as

$$\overline{\text{activity}} = \frac{M_{C_2H_4} \int_0^\tau W_p(t)dt}{C_{Ti} p_{C_2H_4} \tau}, \tag{1}$$