



## Review

Spin-dependent effects in ethylene polymerization with *bis(imino)pyridine iron(II)* complexesBoris Minaev<sup>a, b, \*</sup>, Alina Baryshnikova<sup>b</sup>, Wen-Hua Sun<sup>a, \*\*</sup><sup>a</sup> Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Science, 100190 Beijing, China<sup>b</sup> Organic Chemistry Department, Bohdan Khmelnytsky National University, 18031 Cherkasy, Ukraine

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## ABSTRACT

The general concept of spin-dependent polyethylene polymerization by the *bis(imino)pyridine iron(II)* complexes is presented. It is stressed that the driving force of ethylene polymerization in the presence of *bis(imino)pyridyliron(II)* is a high exothermic effect of the monomer binding to the catalyst in all three low-lying spin states. The origin of low activation barrier in termination reaction between the initial monomolecular ethylene and the growing polyethylene chain corresponds to the energy decreasing of the “ethylene-catalyst” high-spin state complex which correlates directly with the targeted low-spin products through intersystem crossing. The applicability of the spin-catalysis concept to the Brookhart-Gibson catalytic scheme is described in this work on the basis of the detailed analysis of previously published theoretical results of Ziegler's and Morokuma's groups and of recent experimental achievements. The role of the axial-equatorial isomerization in spin-catalysis of Brookhart-Gibson type is discussed in details in connection with the main mechanistic problem of ethylene catalytic polymerization – competition between chain propagation and  $\beta$ -hydrogen atom transfer termination. The original part of review constitutes the calculation of spin-orbit coupling matrix elements in the Brookhart-Gibson catalytic cycle and the discussion of external magnetic field effect on ethylene polymerization.

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## 1. Introduction

In spite of numerous efforts to unravel the mechanism behind early stage of ethylene and propylene polymerization catalyzed by transition-metal complexes the situation is still unclear in some important details [1–18]. Different active species are formed at the beginning of the polymerization process and this variety strongly depends on the reaction conditions. Some of these intermediates are metastable and rapidly transform into the active species for olefin polymerization in the presence of the methylaluminoxane (MAO) cocatalyst [4–15]. Electronic mechanisms of these transformations and spin-dependence of metastable intermediates are of crucial importance for design and engineering of new catalysts being mostly the subject of quantum-chemical calculations.

Important theoretical results have been obtained by Ziegler and Morokuma groups [16,18] at the break of millennium and by more recent studies [10,11,19,20] but the spin-dependence of catalytic activity was not finally understood, elucidated and supported by experimental findings. Meanwhile, the catalysis of controlled selective polymerization of  $\alpha$ -olefins with a wide range of specifications for polymer molecular weight and degree of isomerization is still a demand of chemical industry which can be fulfilled by proper understanding of electronic spin-dependent mechanisms of the chain emergence, initiation, growth and termination.

During last decades development of single-site catalysts has led to a great potential for fine-tuning the microstructure of polyolefins. The polymerization proceeds under the control of both regioselectivity and stereoselectivity requirements which include spin-dependent magnetic and exchange derived interactions. Various types of microstructures and macromolecular backbone architectures can be reached at the conditions of “living polymerization” which occurs when only one species of catalyst provides the growth of one polymer chain.

Unfortunately, the role of electron spin in such mechanisms is not properly discussed so far in order to understand its physical

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reasons and use as the predictive power in the catalysts design. It was just mentioned that for the late-transition metal catalytic complexes (of the Fe and Co ions) the high and low spin states are possible in terms of different computational scheme [6,7,10,15–18] and they are predicted to demonstrate various catalytic activity at the chain propagation and elimination steps of ethylene polymerization. No attempts to analyze this spin-dependent behavior in terms of exchange interaction peculiarity [21–39] and from the spin-catalysis perspective [28–32] have been performed so far in olefin polymerization catalysis.

Meanwhile, in recent decade it is getting more popular and valuable to pay attention to spin effects and two-state reactivity in many catalytic reactions, mostly of biological importance (like in metal-oxo enzymes) [31–37]. Different spin-states reactivity has also important technological aspects including oxidation of hydrocarbons [31] and olefin polymerization [10,27,38] catalyzed by transition-metal compounds which occupy a large segment in the treatment of petroleum-based feedstock in the high-yield chemical industry.

Spin-dependence in catalysis originates from two types of the main physical forces determined by exchange interaction [30] and by weak spin-orbit coupling (SOC) [31]. The late is well-manifested in atomic spectroscopy and photochemistry of metal complexes [21,22]. In catalysis the SOC influence can occur through the multiple catalytic paths differing in the spin state; the non-adiabatic spin inversion induced by SOC can switch, for example, from the ground high-spin state  $^{\lambda}\Psi_0$  to the excited low-spin state  $^{\lambda'}\Psi_0$  ( $\lambda > \lambda'$  are multiplicities,  $\lambda = 2S+1$ ) with smaller activation barrier during chemical transformation which involves the catalyst coordination sphere [31,38]. According to previous results [16,18] and calculations presented here this type of switching can be realized in selective polymerization of  $\alpha$ -olefins with the Brookhart-Gibson catalysts based on *bis*(imino)pyridine ligands [3,9,40–45].

Possibility to change spin during chemical reaction has been generalized as a multistate reactivity concept [34–36] which is especially important in spin-catalysis [30,31]. Originally it was the concept of two-state reactivity being first formulated to account for the gas-phase oxidation of small alkanes by  $\text{FeO}^+$  ion [26,46]. Latter this concept was applied to a wide scope of enzymatic reactions, mostly to oxidation of alkanes by nonheme iron(IV)-oxo complexes [35,36]. In such process the triplet ground state of the starting reactants ( $S = 1$ ,  $\lambda = 3$ ) has a high activation energy; it has been proposed that the oxidation reaction switches to the close-lying quintet spin state ( $S = 2$ ,  $\lambda = 5$ ) due to its lower activation barriers [35,36] and due to SOC-induced mixing between these two states of different spin multiplicity [31]. Thus, the triplet-quintet (T-Q) transition has been postulated to occur in the course of such enzymatic reactions, though SOC calculations have not been performed so far because of complication of the systems involved. But it is possible to analyze SOC effect qualitatively with account of spin-catalysis selection rule [30,31]. If the orbital angular momentum is not changed during the transition between these two states, the SOC integral is equal to zero and spin transition still remains spin-prohibited [31]. The other important rule concerns the requirement that the orbital angular momentum change should occurred at the most heavy atom of the catalytic system – most often on the transition-metal active center [25]. A simple conclusion from these spin-catalysis selection rules is that the multiplicity-changed transition should involve one-electron excitation of the type ( $d_{xz} \rightarrow d_{z^2}$ ) with a simultaneous spin flip [31].

A similar situation seems to occur in ethylene polymerization catalyzed by the iron-bisimine pyridine complexes discovered by the Brookhart's [3] and Gibson's [9] research groups. This discovery of highly efficient catalyst provided a new milestone in academic and industrial researches of homogeneous single-site active species

of new post-metallocene era in polymerization of olefins [10,13]. The type of oxidation state of the metal center and the nature of the active species during the polymerization process are still the matter of discussions [10,11,19,20]. In a number of recent works it was shown that the high-spin (paramagnetic) iron bisimine pyridine complexes of the ferrous and ferric type are active in the ethylene polymerization providing high molecular weight polymers [10,11,19,20]. The detailed DFT calculations by the Ziegler's and Morokuma's groups [16,18] show the importance of the triplet state (at least for the formation of the ethylene insertion stage) for the Fe(II) oxidation state active species. The benchmark DFT results from these two groups differ in various functionals implementation; BP86 was used by Ziegler [18] and B3LYP – by Morokuma's group [16]. The former functional has a strong bias in favor of low-spin singlet state [18]. With account of this divergence in various functionals predictions we want to illustrate application of spin-catalysis approach to the Brookhart-Gibson catalytic scheme and see its possible consequences for chain propagation and chain termination processes in ethylene polymerization. Though the References [16,18] are rather old and consider only the simplified models of the ferrous complexes, they are still very important because of discovering the most essential features of electronic mechanisms behind ethylene polymerization with the Brookhart-Gibson catalysts. The late researches [10,11,19,20] provide important assessments of the relative energy of the Fe(II) and Fe(III) species and the role of various models of the active centers. They consider only high spin states of both ferrous and ferric type catalysts and do not discuss spin dependence in ethylene polymerization. Just Ziegler [18] and Morokuma [16] paid attention to spin-dependent factors which influence the competitive mechanisms of chain growth and termination. Thus, we shall concentrate attention on their results first. Before application to ethylene polymerization catalyzed by the *bis*(imine)pyridine iron complexes we have to consider main principles behind spin-catalysis concept.

## 2. Short description of the spin-catalysis concept

It is shown in a number of DFT calculations [10,16–20,40–43] that the main rate-determining step in ethylene polymerization is the monomer insertion into the metal-alkyl bond; thus, it is bond making process accompanied by bond cleavage. Activation of such simultaneous rearrangements can be treated by a general scheme of spin-catalysis [30–32].

The fundamental role of electron spin in chemistry has been discovered from the first days of quantum mechanics [21]. Even periodicity of the chemical elements depends on spin being determined by the Pauli principle. The quantum nature of covalent chemical bond can not be understood without taking into account the spin properties of electrons [21,22]. In terms of the valence bond (VB) method [37] the exchange integral  $A_{a,b} = \int \int \varphi_a(1)\varphi_b(1)\mathbf{H}\varphi_a(2)\varphi_b(2)d\nu_1d\nu_2$  enters with different signs into the singlet and triplet state energy expressions for overlapping electron pair and stabilizes the former (low-spin) state. Here the atomic orbital (AO)  $\varphi_a(1)$  is a function of the first electron ( $1) = (x_1, y_1, z_1)$ ,  $\mathbf{H}$  is the Hamilton operator. Since spin is the main issue in chemical bonding, it is also crucial in catalysis: the role of catalyst in activation of reactants is to help in promoting spin uncoupling during chemical rearrangement [30,46–49].

The internal electronic structure of a free monomer molecule in gas phase is arranged itself in such a way that it maximizes the intramolecular bonding by proper spin pairing, AOs overlap and exchange attraction. Thus, the interaction with a catalyst involves weakening of internal bond by necessity to provide spin redistribution in order to allow new bonds to be established and this can be exploited to transform the molecule for the desired reaction.

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