COMPUTATIONAL STUDIES ON UNDERSTANDING THE ROLE OF ELECTRON DONORS ON ZIEGLER–NATTA CATALYST ACTIVITY AND PHOTO-OXIDATION BEHAVIOR OF POLYOLEFINS

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Dedicated to

Khatri & Deswal Family

(Late Sh. Rampat Khatri and Smt. Rampyari Rani)

CERTIFICATE

This is to certify that the thesis titled "**COMPUTATIONAL STUDIES ON UNDERSTANDING THE ROLE OF ELECTRON DONORS ON ZIEGLER–NATTA CATALYST ACTIVITY AND PHOTO-OXIDATION BEHAVIOR OF POLYOLEFINS**" is being submitted by **Mr. Vikas Khatri** to the Department of Chemistry, Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy**. This thesis is a record of bonafide research work carried out by him in collaboration with R&D Indian Oil Corporation Limited Faridabad, India under my supervision. In my opinion, the thesis has reached the standards fulfilling the requirements of the regulations relating to the degree. The results contained in this thesis have not been submitted to any other University or Institute for the award of any degree or diploma.

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Vikas Khatri

Abstract

Ziegler-Natta (ZN) catalyst has emerged as an exclusive class of metalorganic catalyst used for the synthesis of stereospecific polyolefins in the beginning of the 1950s. ZN catalyst has high activity as well as gives highly stereospecific product at moderate condition than other metallocene catalysts. Over the years, different generations of ZN catalysts have been discovered and the complexity of the catalyst system has increased with time. Modern ZN catalysts are multicomponent catalysts therefore understanding and modelling is particularly difficult. Nonetheless, the modern catalytic systems have achieved excellent performance levels, allowing for the development of diverse, clean, and cost-effective industrial processes. The studies reporting the structural-activity correlation of electron donors which find applications for the synthesis of a new generation of ZN catalyst with enhanced features have always been the subject of interest for both academicians and industrialists. Furthermore, the successful application and development of these electron donors necessitate a solid fundamental understanding of these interactions that exist between the various components of the ZN catalyst, which is currently lacking. In this thesis, we report DFT investigation to explore different classes of electron donors and photo-degradation behaviour of polyolefins which are the polymerization product of ZN catalyst. In this thesis, the choice of electron donors (internal and external) is not limited to only commercial donors but various functional groups (maleates, carboxylates, succinates, alkoxysilanes) with varying hydrocarbon and functional groups are investigated. Here, we describe a thorough understanding of the interactions (external donor with co-catalyst, internal donor with $TiCl_4$ in presence and absence of $MgCl_2$ support) existing between different components of ZN catalyst. The fundamental understanding of photo-oxidation behavior of different polyolefins ranging from polyethylene to polydecene are also investigated.

The first section of this thesis is devoted to the study of fundamental interactions existing between electron donors and other components of ZN catalyst using both commercial and non-commercial donors. Comparing the experimental FTIR with the computed IR proved the level of theory's validity. The examination of frontier molecular orbitals (FMOs) and natural bond orbitals (NBOs) reveals that charge transfer takes from the electron donor to the acceptor (TEAL and $TiCl_4$) orbitals. In the next section, degradation behavior of different polyolefins and their stability towards photo-oxidation are investigated. An in-depth understanding of different polyolefins and their photo-degradation behaviour are explored.

The detailed understanding of polyolefins gives an idea that the chemical derivatives like unsaturated carbonyl groups which are formed during processing makes them susceptible to photo-degradation and generates microplastic in the ecosystem. Overall, this thesis provides deep insight on the industrial relevant problems, particularly polyolefin industry. The major challenge before polyolefin researchers is how to increase the activity of ZN catalysts by designing new potential electron donors and how to control the degradation of polyolefins which are the polymerization product of ZN catalyst. We have offered a deep understanding of donor-acceptor interactions, as well as a fundamental and simple approach for creating novel electron donors and systematic investigations into the degradation behaviour of various polyolefins that results in the generation of microplastic in ecosystem.

सार

ज़िग्लर-नट्टा (ZN) उत्प्रेरक 1950 के दशक की शुरुआत में स्टीरियो-विशिष्ट पॉलीओलेफ़िन के संश्लेषण के लिए उपयोग किए जाने वाले धातु-कार्बनिक उत्प्रेरक के एक विशेष वर्ग के रूप में उभरा है। ZN उत्प्रेरक में उच्च गतिविधि होती है और साथ ही अन्य मेटालोसीन उत्प्रेरक की तुलना में मध्यम स्थिति में अत्यधिक स्टीरियो-विशिष्ट उत्पाद देता है। इन वर्षों में, ZN उत्प्रेरक की विभिन्न पीढ़ियों की खोज की गई है और समय के साथ उत्प्रेरक प्रणाली की जटिलता में वृद्धि हुई है। आधुनिक ZN उत्प्रेरक बहुघटक उत्प्रेरक हैं इसलिए समझना और मॉडलिंग करना विशेष रूप से कठिन है। बहरहाल, आधुनिक उत्प्रेरक प्रणालियों ने उत्कृष्ट प्रदर्शन स्तर हासिल किए हैं, जिससे विविध, स्वच्छ और लागत प्रभावी औद्योगिक प्रक्रियाओं के विकास की अनुमति मिलती है। इलेक्ट्रॉन दाताओं के संरचनात्मक-गतिविधि सहसंबंध की रिपोर्ट करने वाले अध्ययन, जो उन्नत सुविधाओं के साथ ZN उत्प्रेरक की एक नई पीढ़ी के संश्लेषण के लिए आवेदन पाते हैं, हमेशा शिक्षाविदों और उद्योगपतियों दोनों के लिए रुचि का विषय रहे हैं। इसके अलावा, इन इलेक्ट्रॉन दाताओं के सफल अनुप्रयोग और विकास के लिए ZN उत्प्रेरक के विभिन्न घटकों के बीच मौजूद इन अंतःक्रियाओं की एक ठोस मौलिक समझ की आवश्यकता होती है, जिसका वर्तमान में अभाव है। इस थीसिस में, हम इलेक्ट्रॉन दाताओं के विभिन्न वर्गों और पॉलीओलेफिन के फोटो-डिग्रेडेशन व्यवहार का पता लगाने के लिए डीएफटी जांच की रिपोर्ट करते हैं जो जेडएन उत्प्रेरक के पोलीमराइजेशन उत्पाद हैं। इलेक्ट्रॉन दाताओं (आंतरिक और बाहरी) की पसंद केवल वाणिज्यिक दाताओं तक ही सीमित नहीं है, बल्कि विभिन्न हाइड्रोकार्बन और कार्यात्मक समूहों के साथ विभिन्न कार्यात्मक समूहों (मैलेट, कार्बोक्सिलेट्स, सक्सेनेट, एल्कोक्सीसिलीन) की जांच की जाती है। यहां, हम ZN उत्प्रेरक के विभिन्न घटकों के बीच मौजूद अंतःक्रियाओं (सह-उत्प्रेरक के साथ बाहरी दाता, $TiCl_4$ के साथ आंतरिक दाता की उपस्थिति और $MgCl_2$ समर्थन की अनुपस्थिति) की गहन समझ का वर्णन करते हैं। साथ ही, पॉलीइथाइलीन से लेकर पॉलीडेसीन तक के विभिन्न पॉलीओलेफ़िन के फोटोऑक्सीडेशन व्यवहार की मूलभूत समझ की भी जांच की जाती है।

इस थीसिस का पहला खंड वाणिज्यिक और गैर-वाणिज्यिक दोनों दाताओं का उपयोग करके इलेक्ट्रॉन दाताओं और जेडएन उत्प्रेरक के अन्य घटकों के बीच मौजूद मौलिक बातचीत के अध्ययन के लिए समर्पित है। परिकलित IR के साथ प्रयोगात्मक FTIR की तुलना करने से सिद्धांत की वैधता का स्तर सिद्ध हो गया। फ्रंटियर मॉलिक्यूलर ऑर्बिटल्स (FMOs) और नेचुरल बॉन्ड ऑर्बिटल्स (NBOs) की जांच से इलेक्ट्रॉन डोनर से स्वीकर्ता ऑर्बिटल में चार्ज ट्रांसफर का विस्तार से पता चलता है। अगले खंड में, विभिन्न पॉलीओलेफ़िन के क्षरण व्यवहार और फोटोऑक्सीडेशन के प्रति उनकी स्थिरता की जांच की गई। विभिन्न पॉलीओलेफ़िन और उनके फोटो-डिग्रेडेशन व्यवहार की गहन समझ का पता लगाया गया। पॉलीओलेफिन्स की विस्तृत समझ यह विचार देती है कि असंतृप्त

कार्बोनिल समूह जैसे रासायनिक डेरिवेटिव जो प्रसंस्करण के दौरान बने थे, उन्हें फोटो-डिग्रेडेशन के लिए अतिसंवेदनशील बनाता है और पारिस्थितिकी तंत्र में माइक्रोप्लास्टिक उत्पन्न करता है। कुल मिलाकर, यह थीसिस औद्योगिक प्रासंगिक समस्याओं, विशेष रूप से पॉलीओलेफ़िन उद्योग पर गहरी अंतर्दृष्टि प्रदान करती है। पॉलीओलेफ़िन के सामने बड़ी चुनौती यह है कि वे नए संभावित इलेक्ट्रॉन दाताओं को डिजाइन करके ZN उत्प्रेरक की गतिविधि को कैसे बढ़ा सकते हैं और पॉलीओलेफ़िन के क्षरण को कैसे नियंत्रित कर सकते हैं जो ZN उत्प्रेरक के पोलीमराइज़ेशन उत्पाद हैं। हमने दाता-स्वीकर्ता बातचीत की गहरी समझ की पेशकश की है, साथ ही उपन्यास इलेक्ट्रॉन दाताओं को बनाने के लिए एक मौलिक और सरल दृष्टिकोण और विभिन्न पॉलीओलेफ़िन के क्षरण व्यवहार में व्यवस्थित जांच की पेशकश की है जिसके परिणामस्वरूप पारिस्थितिक तंत्र में माइक्रोप्लास्टिक उत्पन्न होता है।

Permissions

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List of Publications Related to Work Presented in this Thesis as on Thesis Submission Date

1. **Vikas Khatri**, Usharani Sahoo, Sukhdeep Kaur, Rashmi Rani, Gurmeet Singh, Gurpreet Singh Kapur and Hemant K. Kashyap, Control of Ziegler–Natta Catalyst Activity by the Structural Design of Alkoxysilane-based External Donors, *New J. Chem.*, **44**, 6845 (2016).
2. **Vikas Khatri**, Harender S. Dhattarwal, Hemant K. Kashyap, and Gurmeet Singh, First-principles based Theoretical Investigation of Impact of Polyolefin Structure on Photo-oxidation Behavior, *J. Comput. Chem.*, **42**, 1710 (2021).
3. **Vikas Khatri**, Harender S. Dhattarwal, Gurmeet Singh, and Hemant K. Kashyap, First-principles based Computational Evaluation of Binding Modes of Internal Donors with Titanium Tetrachloride, *J. Comput. Chem.* (**Submitted**).

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