Catalytic Transformation of Hydrocarbons to Valorized Products on Nanoclusters

Iqra

Department of Chemical Engineering
Indian Institute of Technology Delhi
Hauz Khas, New Delhi – 110016
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Iqra

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To my beloved mother, Mrs. Mymoona

Whose unwavering love, sacrifices, and endless prayers
have been the foundation of all my achievements.

CERTIFICATE

This is to certify that the thesis entitled "**Catalytic Transformation of Hydrocarbons to Valorized Products on Nanoclusters**" is being submitted by **Ms IQRA** to the Indian Institute of Technology Delhi for the award of the degree of **DOCTOR OF PHILOSOPHY**. This is a record of bonafide research work carried out by her under our supervision and guidance. The matter presented in this thesis has not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.

Prof M. Ali Haider
Professor,
Department of Chemical Engineering,
Indian Institute of Technology, Delhi,
Hauz Khas, New Delhi- 110016

Prof. Kamal K Pant
Professor,
Department of Chemical Engineering,
Indian Institute of Technology, Delhi,
Hauz Khas, New Delhi- 110016

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"Indeed, with hardship comes ease." *– Surah Ash-Sharh (94:6)*

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ABSTRACT

Nanoclusters have attracted significant interest as catalysts due to their unique physical and chemical properties, which significantly differ from those of bulk materials. Their high surface-to-volume ratio and tunable electronic structures enable enhanced catalytic performance, making them promising candidates for hydrocarbon transformation. Efficient catalytic transformation of hydrocarbons into value-added chemicals is essential for sustainable chemical production, addressing both economic and environmental concerns. However, achieving high selectivity and stability in these transformations remains a challenge, requiring a deeper understanding of catalytic mechanisms at the atomic level. This thesis aims to elucidate the mechanisms by which transition metal nanoclusters facilitate hydrocarbon catalytic transformation into value-added chemicals. The focus is on three key areas of research: the dehydrogenation of hydrocarbons into value-added chemicals using metal carbide nanoclusters and metal oxide nanoclusters encapsulated in zeolite, the hydrogenation of unsaturated hydrocarbon compounds using metal sulphide nanoclusters and the conversion of polyolefins into fuels using metal nanoclusters. A combination of density functional theory (DFT) and molecular dynamics (MD) simulations is employed to gain atomic-level insights, complementing experimental findings.

The first study investigates the mechanistic insights for methane dehydroaromatization (MDA) reaction on nanocluster isomers using DFT and MD simulations. An investigation is carried out into the catalytic behaviour of two distinct isomers of molybdenum (Mo) carbide nanoclusters confined within the zeolite (ZSM-5) cage. The significance of metastable nanoclusters, the possible key intermediate and the mechanisms behind ethylene and acetylene formation have been elucidated, illustrating

that higher energy Mo carbide structures are helpful for C-H activation and C-C coupling. Furthermore, the synthesis of nanoclusters from two different precursors, i.e. hexagonal (h-MoO_3) and orthorhombic (α-MoO_3) crystals of molybdenum oxide is studied. The catalyst prepared from the metastable hexagonal form (h-MoO_3) on the zeolite support measured a higher benzene formation rate and reduced coke deposition compared to α-MoO_3/HZSM-5. The simulations reveal greater interaction and facile anchoring of h-MoO_3 with the zeolite surface. This interaction during the impregnation process led to the formation of more active molybdenum carbide nanoclusters responsible for C-H activation and C-C coupling.

The second study focuses on the reactivity of nanoclusters for the conversion of methane to value-added chemicals, specifically the selective formation of formic acid. Atomically dispersed Fe and Au within Na ZSM-5 catalyst produced C_1 oxygenates with 95 % selectivity to formic acid. This highly selective product synthesis is attributed to the synergistic effect between the Fe and Au species. DFT simulations reveal insights into the mechanism of methane transformation to formic acid on nanoclusters encapsulated in ZSM-5, emphasising the roles of gold (Au) and sodium (Na) in influencing reaction pathways. The active site is identified as a mononuclear Fe cluster anchored on the Al-O acidic site, which lies in close proximity to cationic gold species. Surface hydroxyl on the Au nanoparticle was identified as facilitating the O-H and C-H activation reactions in methanol, forming formic acid.

The third study examines the effect of alkali metal cations (Li^+, Na^+, K^+, Rb^+, and Cs^+) in ethylene hydrogenation. A detailed mechanistic pathway is investigated to compute adsorption energies, reaction energies, and activation barriers for elementary steps in the hydrogenation process. To understand the observed trends, the study incorporates

charge analysis and computationally derived IR spectroscopy to highlight the electronic and structural differences among the cations. The results highlight the role of cation size and electronic properties in influencing catalytic performance, supported by experimental validation.

The final study explores the catalytic activation of polyolefins to fuels using Lewis acid nanocluster catalysts, particularly N-butyl pyridine chloride and anhydrous aluminium chloride ($AlCl_3$), along with copper chloride and iron chloride nanoclusters. Notably, Fe^{3+} and Cu^{2+} showed effective conversion rates in LDPE (low-density polyethene) experimentally. Further, DFT results provide insights into the role of these metal chlorides, suggesting that $CuCl_2$ and $FeCl_3$ facilitate the formation of reactive nanoclusters that dissociate more effectively in $AlCl_3$, the proposed active site, thereby enhancing conversion and improving product selectivity. This thesis provides fundamental insights into the mechanistic pathways of nanocluster-mediated hydrocarbon transformations by integrating theoretical studies with experimental validation. The findings advance the understanding of catalytic processes for fuel and chemical production.

सार

नैनोक्लस्टर अपने अद्वितीय भौतिक और रासायनिक गुणों के कारण उत्प्रेरकों के रूप में महत्वपूर्ण रुचि प्राप्त कर चुके हैं, जो थोक सामग्री से काफी भिन्न होते हैं। यह शोध प्रबंध इस बात को स्पष्ट करने का प्रयास करता है कि संक्रमण धातु नैनोक्लस्टर हाइड्रोकार्बन के उत्प्रेरित रूपांतरण को मूल्य वर्धित रसायनों में कैसे सक्षम बनाते हैं। शोध के प्रमुख क्षेत्रों में मीथेन में C-H बंधों का सक्रियण, असंतृप्त यौगिकों का हाइड्रोजनेशन और पॉलीओलेफिन्स का ईंधन में रूपांतरण शामिल हैं। इस अध्ययन में घनत्व कार्यात्मक सिद्धांत (DFT) और आणविक गतिकी (MD) सिमुलेशन का उपयोग करके आणविक स्तर पर अंतर्दृष्टि प्राप्त की गई है, जो प्रयोगात्मक निष्कर्षों का पूरक है।

पहले अध्ययन में, मीथेन डिहाइड्रोएरोमैटाइजेशन (MDA) प्रतिक्रिया के लिए नैनोक्लस्टर आइसोमर्स पर यांत्रिक अंतर्दृष्टि की जांच की गई, जिसमें DFT और MD सिमुलेशन का उपयोग किया गया। ज़ियोलाइट (ZSM-5) पिंजरे में एंकर किए गए मोलीब्डेनम (Mo) कार्बाइड नैनोक्लस्टर के दो अलग-अलग आइसोमर्स के उत्प्रेरक व्यवहार का अवलोकन किया गया। संभावित मध्यवर्ती अवस्थाओं, मेटास्टेबल नैनोक्लस्टर के महत्व और इथाइलीन निर्माण तंत्र को स्पष्ट किया गया, जिससे यह पता चला कि उच्च ऊर्जा वाले Mo कार्बाइड संरचनाएं C-H सक्रियण और C-C युग्मन के लिए अधिक प्रभावी होती हैं। इसके अतिरिक्त, दो अलग-अलग हेक्सागोनल ($h\text{-}MoO_3$) और ऑर्थोरोम्बिक ($\alpha\text{-}MoO_3$) मोलीब्डेनम ऑक्साइड क्रिस्टलों से नैनोक्लस्टर के संश्लेषण का अध्ययन किया गया। मेटास्टेबल हेक्सागोनल MoO_3 ($h\text{-}MoO_3$) से निर्मित उत्प्रेरक ने बेंजीन उत्पादन दर में वृद्धि और कोक जमाव में कमी का प्रदर्शन किया। MD और DFT सिमुलेशन से पता चला कि $h\text{-}MoO_3$ ज़ियोलाइट सतह के साथ अधिक प्रभावी ढंग से इंटरैक्ट

करता है, जिससे अधिक सक्रिय मोलीब्डेनम कार्बाइड नैनोक्लस्टर बनते हैं, जो C-H सक्रियण और C-C युग्मन के लिए जिम्मेदार होते हैं।

दूसरे अध्ययन में, मीथेन के मूल्य वर्धित रसायनों में रूपांतरण, विशेष रूप से फॉर्मिक एसिड के चयनात्मक उत्पादन की जांच की गई। Na-ZSM-5 में परमाणु स्तर पर विभक्त Fe और Au का उपयोग करके 95% चयनात्मकता के साथ C_1 ऑक्सीजन यौगिकों का उत्पादन किया गया। यह उच्च चयनात्मकता Fe और Au प्रजातियों के सहक्रियात्मक प्रभाव के कारण देखी गई। DFT सिमुलेशन से यह स्पष्ट हुआ कि Fe को Al-O अम्लीय स्थलों पर एंकर किया जाता है, जबकि समीपस्थ कैटायनिक Au प्रजातियां O-H और C-H सक्रियण को सक्षम बनाती हैं। Au सतह पर उपस्थित हाइड्रॉक्सिल समूहों ने मीथनॉल के ऑक्सीकरण में सहायता की, जिससे फॉर्मिक एसिड का चयनात्मक निर्माण हुआ। यह अध्ययन धातु-समर्थन अंतःक्रियाओं और सह-उत्प्रेरक प्रभावों के महत्व को उजागर करता है।

तीसरे अध्ययन में, क्षार धातु कैटायनों (Li^+, Na^+, K^+, Rb^+, और Cs^+) के इथाइलीन हाइड्रोजनेशन पर प्रभाव की जांच की गई। एक विस्तृत यांत्रिक मार्ग को मॉडल किया गया, जिसमें अवशोषण ऊर्जा, प्रतिक्रिया ऊर्जा, और सक्रियण अवरोधों की गणना की गई। आवेश विश्लेषण और अवरक्त (IR) स्पेक्ट्रोस्कोपी का उपयोग कैटायन-निर्भर प्रतिक्रियाशीलता को समझने के लिए किया गया। परिणामों से पता चला कि कैटायन का आकार और उसकी इलेक्ट्रॉनिक विशेषताएं उत्प्रेरक की गतिविधि और चयनात्मकता को प्रभावित करती हैं, जिसे प्रयोगात्मक निष्कर्षों से समर्थित किया गया।

अंतिम अध्ययन में, पॉलीओलेफिन्स को ईंधन में परिवर्तित करने के लिए लुईस एसिड नैनोक्लस्टर उत्प्रेरकों का अध्ययन किया गया। विशेष रूप से N-ब्यूटाइल पाइरीडिन क्लोराइड और निर्जल

एल्युमिनियम क्लोराइड ($AlCl_3$), साथ ही कॉपर क्लोराइड ($CuCl_2$) और आयरन क्लोराइड ($FeCl_3$) नैनोक्लस्टर की प्रभावशीलता का मूल्यांकन किया गया। Fe^{3+} और Cu^{2+} ने LDPE (लो-डेंसिटी पॉलीएथिलीन) के प्रभावी रूपांतरण का प्रदर्शन किया। DFT निष्कर्षों से पता चला कि $CuCl_2$ और $FeCl_3$ सक्रिय नैनोक्लस्टर के निर्माण को बढ़ावा देते हैं, जो $AlCl_3$ में अधिक प्रभावी ढंग से अलग हो जाते हैं, जिससे रूपांतरण और चयनात्मकता में सुधार होता है।

यह शोध प्रबंध नैनोक्लस्टर-मध्यस्थ हाइड्रोकार्बन रूपांतरण के यांत्रिक मार्गों की मौलिक अंतर्दृष्टि प्रदान करता है, जिसमें गणनात्मक मॉडलिंग को प्रयोगात्मक निष्कर्षों द्वारा समर्थित किया गया है। इस अध्ययन से उत्प्रेरक प्रक्रियाओं, ईंधन उत्पादन, और कार्बन उपयोगीकरण की समझ में महत्वपूर्ण प्रगति होती है।

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