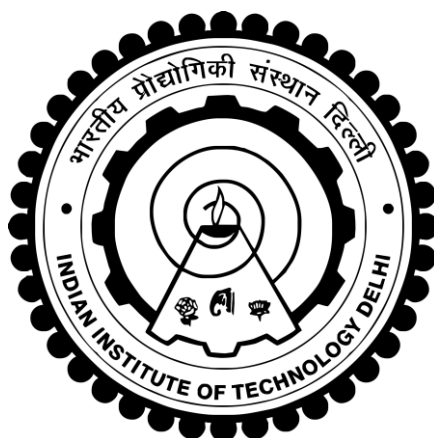


**UNDERSTANDING CATALYSIS BY MOLYBDENUM
CARBIDE NANOCLUSTERS IN Mo/HZSM-5 CATALYST
FOR METHANE DEHYDROAROMATIZATION**

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**DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
JULY 2021**

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by

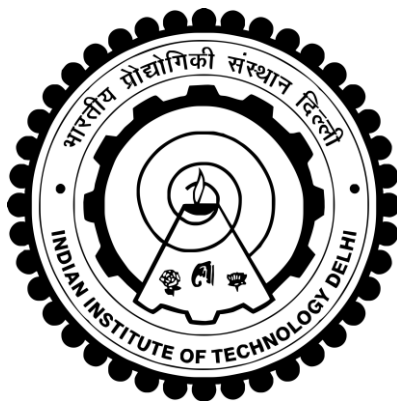
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Submitted

in fulfillment of the requirements of the degree of Doctor of philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI
July 2021

Dedicated to my Parents

Kiran Pal Singh and Prem Lata

Without whom this journey would have been incomplete

CERTIFICATE

This is to certify that the thesis titled “**UNDERSTANDING CATALYSIS BY MOLYBDENUM CARBIDE NANOCCLUSERS IN Mo/HZSM-5 CATALYST FOR METHANE DEHYDROAORMATIZATION**” being submitted by **Mr. Sonit Balyan** to the Indian Institute of Technology Delhi for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by him. **Mr. Sonit Balyan** has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard. The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

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SONIT BALYAN

ABSTRACT

Single step methane conversion to value added products is an economical route to exploit natural gas reservoirs from industrial perspective. Conversion of methane to aromatics in non-oxidative conditions generally utilizes a bifunctional catalyst having active molybdenum species supported on zeolite (Mo/HZSM-5). In this reaction, the nature of the active site for methane on Mo is suggested to be a carbide (or an oxycarbide) and the catalyst is known to deactivate from carbon deposition over time due to the formation of polyaromatic hydrocarbons. The evolution of the molybdenum carbide species from the precursor oxide and oxycarbide forms, dictating the anchoring of the carbide cluster on the zeolite support, is considered the key aspect in deciding the extent of coke formation on the catalyst. Herein, density functional theory (DFT) calculations are utilized to study the catalytically active carbide (Mo_xCy) clusters in C-H bond activation and C-C coupling reaction to form C_2 intermediates. A massively parallel cascade genetic algorithm (cGA) is applied to scan the potential energy surface (PES) for all possible low-energy structures (including the global minimum) of Mo_xCy . Catalytic activity of the global minimum and metastable clusters are assessed as well as compared for methane activation, highlighting the role of metastable clusters influencing the overall reaction rates. The mechanistic insights obtained from DFT calculations thus provides a molecular level engineering approach wherein, the catalyst is rationally synthesized to obtain desired active sites anchored on the zeolite support. These active sites are stable and responsible for providing high aromatic selectivity and the overall reactivity. This is implemented in experiments at three stages; a) this is achieved by obtaining a higher amount of Mo carbide by tailoring the carburizing agent. Changing the carburizing condition from pure methane to a mixture of hydrocarbon gases (mimicking the natural gas).

In this reference, we studied the effect of mixture of C_2H_6 , C_3H_8 , C_4H_{10} , and methane along with hydrogen on molybdenum carbide formation during the initial carburization step; b) another strategy to stabilize these primary molybdenum oxide/carbide species over the zeolite after subsequent thermal and chemical treatment is proposed. It is achieved by thermal treatment of molybdenum precursors and conversion of orthorhombic α - MoO_3 to metastable hexagonal h - MoO_3 via hydrothermal topotactic transformation. In this work, the role of Mo precursor interaction with the zeolite in altering catalyst reactivity is studied; and c) in order to achieve higher aromatic (benzene) selectivity the brønsted acidity of HZSM-5 zeolite is moderated by pretreating it with boric acid. Moreover, this novel strategy of controlling the brønsted acidity of HZSM-5 zeolite enhances catalyst stability in MDA by reducing the agglomeration of active Mo_2C_6 species and the carbon deposition. Overall, through these studies, the dissertation provides molecular level insights of the active catalyst sites of the reaction. Nonetheless, this study provides a guiding tool for rational catalyst design by specifying the choice of Mo precursor, carburizing conditions and zeolite treatment for obtaining desired reactivity and product selectivity, with a potential to achieve higher catalyst stability for MDA process.

सार

औद्योगिक दृष्टिकोण से प्राकृतिक गैस के भंडार को मीथेन के एकल चरण में मूल्य वर्धित उत्पादों में परिवर्तन करना एक किफायती मार्ग है। गैर-ऑक्सीडेटिव स्थितियों में मीथेन का एरोमेटिक्स में रूपांतरण आम तौर पर जिओलाइट ($\text{Mo}/\text{HZSM-5}$) पर स्थित द्वि-कार्यात्मक उत्प्रेरक मौजूद सक्रिय मोलिब्डेनम स्थलों का उपयोग करता है। यह माना जाता है की इस प्रतिक्रिया में, मोलिब्डेनम पर मीथेन के लिए सक्रिय स्थलों की प्रकृति को कार्बाइड (या एक ऑक्सीकार्बाइड) है और समय के साथ उत्प्रेरक की सतह पर पॉलीएरोमैटिक हाइड्रोकार्बन के गठन के कारण कार्बन जमाव से उत्प्रेरक निष्क्रिय हो जाता है। मोलिब्डेनम कार्बाइड अणुओं का ऑक्साइड और ऑक्सीकार्बाइड के रूपों से विकास, जिओलाइट नींव पर कार्बाइड क्लस्टर के लंगर को निर्धारित करता है और यह माना जाता है की उत्प्रेरक पर कोक गठन की सीमा तय करने में महत्वपूर्ण पहलू है। इस प्रकार, घनत्व कार्यात्मक सिद्धांत (DFT) गणनाओं का उपयोग C-H बंधन और C-C युग्मन प्रतिक्रिया से C_2 मध्यवर्ती बनाने के लिए उत्प्रेरक सक्रिय कार्बाइड (Mo_xC_y) समूहों का अध्ययन किया गया है। Mo_xC_y की सभी संभावित कम-ऊर्जा संरचनाओं (वैश्विक न्यूनतम सहित) के लिए संभावित ऊर्जा सतह (PES) की जाँच करने के लिए एक व्यापक समानांतर कैस्केड आनुवंशिक एल्गोरिथ्म (cGA) इस्तेमाल किया जाता है। वैश्विक न्यूनतम और मेटास्टेबल समूहों की उत्प्रेरक गतिविधि का मूल्यांकन किया जाता है और साथ ही मीथेन सक्रियण की तुलना में, समग्र प्रतिक्रिया दरों को प्रभावित करने वाले मेटास्टेबल समूहों की भूमिका पर प्रकाश डाला गया है। डीएफटी गणनाओं से प्राप्त यांत्रिकी अंतर्दृष्टि इस प्रकार एक आणविक स्तर इंजीनियरिंग दृष्टिकोण प्रदान करती है, जिसमें जिओलाइट समर्थन पर लगी वांछित सक्रिय साइटों को प्राप्त करने के लिए उत्प्रेरक को तर्कसंगत रूप से संश्लेषित किया जाता है। ये सक्रिय साइटें एरोमेटिक्स चयनात्मकता और समग्र प्रतिक्रियाशीलता प्रदान करने के लिए स्थिर और जिम्मेदार हैं। इसे तीन चरणों में प्रयोगों में लागू किया

गया है; क) यह कार्बराइजिंग प्रतिनिधि का अनुरूपण करके अधिक मात्रा में मोलिब्डेनम कार्बाइड प्राप्त करके प्राप्त किया जाता है। शुद्ध मीथेन से कार्बराइजिंग स्थिति को हाइड्रोकार्बन गैसों के मिश्रण में बदलना (प्राकृतिक गैस की नकल करना)। इस संदर्भ में, हमने प्रारंभिक कार्बराइजेशन चरण के दौरान मोलिब्डेनम कार्बाइड के गठन पर हाइड्रोजन के साथ C_2H_6 , C_3H_8 , C_4H_{10} और मीथेन के मिश्रण के प्रभाव का अध्ययन किया है। ख) बाद के उष्ण और रासायनिक उपचार के बाद जिओलाइट पर इन प्राथमिक मोलिब्डेनम ऑक्साइड/कार्बाइड प्रजातियों को स्थिर करने के लिए एक और रणनीति प्रस्तावित है। यह मोलिब्डेनम अग्रदूतों के उष्ण उपचार और ऑर्थोरोम्बिक $\alpha\text{-MoO}_3$ को हाइड्रोथर्मल टोपोटैक्टिक परिवर्तन के माध्यम से मेटास्टेबल हेक्सागोनल $h\text{-MoO}_3$ में परिवर्तित करके प्राप्त किया जाता है। इस काम में, उत्प्रेरक प्रतिक्रियाशीलता को बदलने में जिओलाइट के साथ मोलिब्डेनम पूर्वगामी परस्पर क्रिया की भूमिका का अध्ययन किया गया है; तथा ग) उच्च एरोमैटिक (बेंजीन) चयनात्मकता प्राप्त करने के लिए HZSM-5 जिओलाइट की ब्रॉस्टेड अम्लता को बोरिक एसिड के साथ प्रीट्रीट करके नियंत्रित किया जाता है। इसके अलावा, HZSM-5 जिओलाइट की ब्रॉस्टेड अम्लता को नियंत्रित करने की यह नई रणनीति सक्रिय Mo_2C_6 अणुओं के समूह और कार्बन जमाव को कम करके MDA में उत्प्रेरक स्थिरता को बढ़ाती है। कुल मिलाकर, इन अध्ययनों के माध्यम से, शोध प्रबंध प्रतिक्रिया के सक्रिय उत्प्रेरक साइटों के आणविक स्तर की अंतर्दृष्टि प्रदान करता है। बहरहाल, यह अध्ययन MDA प्रक्रिया के लिए उच्च उत्प्रेरक स्थिरता प्राप्त करने की क्षमता के साथ, वांछित प्रतिक्रियाशीलता और उत्पाद चयनात्मकता प्राप्त करने के लिए मोलिब्डेनम अग्रदूत, कार्बराइजिंग स्थितियों और जिओलाइट उपचार की पसंद को निर्दिष्ट करके तर्कसंगत उत्प्रेरक डिजाइन के लिए एक मार्गदर्शक उपकरण प्रदान करता है।

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Acronyms

Å	Angstrom
atm	Atmosphere
BET	Brunauer–Emmett–Teller
BJH	Barrett-Joyner-Halenda
FWHM	Full width at half maximum
FT-IR	Fourier Transform Infrared Spectroscopy
GHSV	Gas hourly space velocity
h	Hour
JCPDS	Joint Committee on Powder Diffraction Standards
nm	Nanometer
PSD	Particle size distribution
SAXS	Small angle X-ray scattering
SEM	Scanning electron spectroscopy
STP	Standard temperature and pressure
TCD	Thermal conductivity detector
TEM	Transmission electron spectroscopy
TGA	Thermo-gravimetric analysis
TOS	Time on stream
TPD	Temperature programmed desorption
TPO	Temperature programmed oxidation
TPR	Temperature programmed reduction
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction