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THE UNIVERSITY
OF QUEENSLAND
AUSTRALIA

**INVESTIGATING THE ROLE OF SUPPORT POROSITY,
ACIDITY, AND PROMOTERS EFFECT FOR Mo/HZSM-5
CATALYST IN METHANE DEHYDROAROMATIZATION
REACTION**

by

Deepti Mishra

Submitted

in fulfillment of the requirements for the joint degree of

DOCTOR OF PHILOSOPHY

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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THE UNIVERSITY OF QUEENSLAND

MARCH 2024

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Dedicated to my Parents

Shivdev Mishra and Prabha Mishra

Without whom this Ph.D. journey would have been incomplete

Supervisor Certification

This is to certify that the thesis entitled “**Investigating the role of support porosity, acidity and promoters’ effect for Mo/HZSM-5 catalyst in methane dehydroaromatization reaction**” being submitted by **Ms. Deepti Mishra** to the Indian Institute of Technology Delhi and The University of Queensland for the award of the degree of **Doctor of Philosophy** is a record of *bonafide* research work carried out by her. **Ms. Deepti Mishra** has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to our 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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Abstract

The abundance of natural gas reserves and tremendous progress in its production has drawn great interest from the research community to develop a suitable technology for the utilization of stranded natural gas, into transportable chemicals/fuels which are of great commercial value. Catalytic transformation of the simplest hydrocarbon methane into easily transportable hydrocarbons such as benzene and aromatics in oxygen-free conditions is of significant importance that affords an alternate path for the utilization of methane to fulfill the growing energy demand. Mo-exchanged zeolite (ZSM-5) is an extensively recognized catalyst for this reaction that behaves in a bifunctional manner providing active sites for methane activation and benzene formation. The major challenge associated with thermodynamic restraint methane dehydroaromatization (MDA) using molybdenum-impregnated HZSM-5 zeolite (Mo/HZSM-5) catalyst is the generation of an extensive amount of coke inside the sole micropores and over the surface which leads to the deactivation of the catalyst within a few hours. These problems require more insights into the development of suitable MDA catalysts with improved catalytic activity in view of upgrading the process to a commercial level. In this context, the present research covers the introduction of hierarchical zeolite comprised of unique micro/mesoporous structures that can assist in delivering homogeneous Mo dispersion while the additional pores accelerate the mass transfer of reactant and formed benzene products. With this approach, the first study deals with the synthesis of hierarchical ZSM-5 support *via* applying a dual template soft templating strategy and its application for the MDA reaction. Another factor that affects the MDA catalytic activity is the dispersibility and stability of active molybdenum species under the reaction condition. A strategy to stabilize the Mo-oxide precursor over the zeolite support is proposed and, in this regard, two different forms of MoO_3 (α - MoO_3 , h- MoO_3) were synthesized and applied as Mo precursors for the synthesis of microwave (MW) assisted Mo/HZSM-5 catalysts. The correspondence

between the impact of different Mo oxide precursors and their preparation method on the catalytic activity of Mo/HZSM-5 was established for the non-oxidative MDA process that provides maximum benzene selectivity with affordable stability. In order to reduce the coke generation inside the zeolite support, the Bronsted acidity of HZSM-5 zeolite is moderated by substituting trivalent Al atom with various heteroatoms (V, B, Ga, & Fe). Modification in Bronsted acidic sites of zeolite in Mo/MFI catalyst showed improved stability towards MDA by reducing the coke deposition thus extending the catalyst lifetime. In parallel efforts, ceria-zirconia mixed oxides as an oxygen transfer agent along with Mo/HZSM-5 to improve the catalytic stability by performing the *in-situ* hydrogen oxidation reaction was accomplished which in turn improved the methane conversion (11% initially) and benzene selectivity (70%) at 90-120 minutes of MDA reaction. Additionally, the promotional role of Ag and its addition with Mo/HZSM-5 catalysts were explored to improve the MDA catalytic activity and stability. Investigation revealed that the co-impregnation of Ag with Mo/HZSM-5 significantly increases the total acidity (7.8%) and hence aromatization ability of the catalyst thereby providing a higher benzene formation rate (320 nmol/gcat. s), with a decreased amount of coke generation over the catalyst surface. Performed characterization showed that Ag addition modified the chemical environment of Mo/HZSM-5 which possesses superior catalytic activity towards MDA. Overall, this dissertation focused on developing a suitable MDA catalyst *via* modifying the support porosity, acidity, Mo precursor's state, and promoter's effect to reduce the coke formation with simultaneous improvement in benzene productivity toward methane aromatization.

सार

प्राकृतिक गैस भंडार की प्रचुरता और इसके उत्पादन में जबरदस्त प्रगति ने फंसे हुए प्राकृतिक गैस के परिवहन योग्य रसायनों/ईंधन में उपयोग के लिए एक उपयुक्त तकनीक विकसित करने के लिए अनुसंधान समुदाय में काफी रुचि पैदा की है, जो कि बड़े वाणिज्यिक मूल्य के हैं। सरलतम हाइड्रोकार्बन मीथेन का आसानी से परिवहन योग्य हाइड्रोकार्बन जैसे बेंजीन और एरोमैटिक्स में ऑक्सीजन मुक्त स्थितियों में उत्प्रेरक परिवर्तन महत्वपूर्ण महत्व रखता है जो बढ़ती ऊर्जा मांग को पूरा करने के लिए मीथेन के उपयोग के लिए एक वैकल्पिक मार्ग प्रदान करता है। मो-एक्सचेंज्ड जिओलाइट (ZSM-5) इस प्रतिक्रिया के लिए एक व्यापक रूप से मान्यता प्राप्त उत्प्रेरक है जो मीथेन सक्रियण और बेंजीन गठन के लिए सक्रिय साइट प्रदान करने वाले द्वि-कार्यात्मक तरीके से व्यवहार करता है। मोलिब्डेनम-संसेचित HZSM-5 जिओलाइट (Mo/HZSM-5) उत्प्रेरक का उपयोग करके थर्मोडायनामिक संयम मीथेन डीहाइड्रोएरोमेटाइजेशन (एमडीए) से जुड़ी प्रमुख चुनौती एकमात्र माइक्रोप्रोर्स के अंदर और सतह पर व्यापक मात्रा में कोक का उत्पादन है जो निष्क्रियता की ओर ले जाती है। कुछ ही घंटों में उत्प्रेरक का। इन समस्याओं के लिए प्रक्रिया को व्यावसायिक स्तर पर अपग्रेड करने के मद्देनजर बेहतर उत्प्रेरक गतिविधि के साथ उपयुक्त एमडीए उत्प्रेरक के विकास में अधिक अंतर्दृष्टि की आवश्यकता है। इस संदर्भ में, वर्तमान शोध में अद्वितीय सूक्ष्म/मेसोपोरस संरचनाओं से युक्त पदानुक्रमित जिओलाइट की शुरुआत को शामिल किया गया है जो सजातीय मो फैलाव प्रदान करने में सहायता कर सकता है जबकि अतिरिक्त छिद्र प्रतिक्रियाशील और गठित बेंजीन उत्पादों के बड़े पैमाने पर स्थानांतरण में तेजी लाते हैं। इस दृष्टिकोण के साथ, पहला अध्ययन दोहरे टेम्पलेट सॉफ्ट टेम्पलेटिंग रणनीति को लागू करने और एमडीए प्रतिक्रिया के लिए इसके अनुप्रयोग के माध्यम से पदानुक्रमित ZSM-5 समर्थन के संश्लेषण से संबंधित है। एक अन्य कारक जो एमडीए उत्प्रेरक गतिविधि को प्रभावित करता है वह प्रतिक्रिया स्थिति के तहत सक्रिय मोलिब्डेनम प्रजातियों की फैलावशीलता और स्थिरता है। जिओलाइट समर्थन पर मो-ऑक्साइड अग्रदूत को स्थिर करने की एक रणनीति प्रस्तावित है और, इस संबंध में, MoO_3 ($\alpha\text{-MoO}_3$, $h\text{-MoO}_3$) के दो अलग-अलग रूपों को संश्लेषित किया गया और माइक्रोवेव (MW) के संश्लेषण के लिए Mo अग्रदूतों के रूप में लागू किया विभिन्न Mo ऑक्साइड अग्रदूतों के प्रभाव और Mo/ZHSM-5 की उत्प्रेरक गतिविधि पर उनकी तैयारी विधि के बीच पत्राचार गैर-ऑक्सीडेटिव एमडीए प्रक्रिया के लिए स्थापित किया गया था जो किफायती स्थिरता के साथ अधिकतम बेंजीन चयनात्मकता प्रदान करता है। जिओलाइट समर्थन के अंदर कोक उत्पादन को कम करने के लिए, HZSM-5 जिओलाइट की ब्रॉस्टेड अम्लता को त्रिसंयोजक अल परमाणु को विभिन्न हेटेरोएटम (वी, बी, गा, और फ़े) के साथ प्रतिस्थापित करके नियंत्रित किया जाता है। एमओ/एमएफआई उत्प्रेरक में

जिओलाइट के ब्रॉस्टेड अम्लीय साइटों में संशोधन ने कोक जमाव को कम करके एमडीए के प्रति बेहतर स्थिरता दिखाई, जिससे उत्प्रेरक का जीवनकाल बढ़ गया। समानांतर प्रयासों में, सेरिया-ज़िरकोनिया ने इन-सीटू हाइड्रोजन ऑक्सीकरण प्रतिक्रिया करके उत्प्रेरक स्थिरता में सुधार करने के लिए Mo/HZSM-5 के साथ ऑक्सीजन ट्रांसफर एजेंट के रूप में ऑक्साइड को मिश्रित किया, जिसके परिणामस्वरूप मीथेन रूपांतरण में सुधार हुआ (शुरुआत में 11%) और एमडीए प्रतिक्रिया के 90-120 मिनट पर बेंजीन चयनात्मकता (70%)। इसके अतिरिक्त, एमडीए उत्प्रेरक गतिविधि और स्थिरता में सुधार के लिए एजी की प्रचार भूमिका और एमओ/एचजेडएसएम-5 उत्प्रेरक के साथ इसके जुड़ाव का पता लगाया गया। जांच से पता चला कि Mo/HZSM-5 के साथ Ag के सह-संसेचन से कुल अम्लता (7.8%) काफी बढ़ जाती है और इसलिए उत्प्रेरक की सुगंधीकरण क्षमता कम हो जाती है, जिससे उच्च बेंजीन निर्माण दर (320 nmol/gcat. s) मिलती है। उत्प्रेरक सतह पर कोक उत्पादन की मात्रा। प्रदर्शन किए गए लक्षण वर्णन से पता चला कि एजी के अतिरिक्त ने Mo/HZSM-5 के रासायनिक वातावरण को संशोधित किया है जिसमें एमडीए के प्रति बेहतर उत्प्रेरक गतिविधि है। कुल मिलाकर, यह शोध प्रबंध मीथेन सुगंधीकरण की दिशा में बेंजीन उत्पादकता में एक साथ सुधार के साथ कोक गठन को कम करने के लिए समर्थन सरंध्रता, अम्लता, मो अग्रदूत की स्थिति और प्रमोटर के प्रभाव को संशोधित करके एक उपयुक्त एमडीए उत्प्रेरक विकसित करने पर केंद्रित है।

Declaration by author

This thesis is composed of my original work and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution by others to jointly authored works that I have included in my thesis.

I have clearly stated the contribution of others to my thesis as a whole, including statistical assistance, survey design, data analysis, significant technical procedures, professional editorial advice, financial support, and any other original research work used or reported in my thesis. The content of my thesis is the result of work I have carried out since the commencement of my higher degree by research candidature and does not include a substantial part of work that has been submitted to qualify for the award of any other degree or diploma in any university or other tertiary institution. I have clearly stated which parts of my thesis, if any, have been submitted to qualify for another award.

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Publications included in this thesis

1. Mishra, D., Mishra, S., Modak, A., Pant, K.K., Zhao, X.S., 2022a. Hierarchically modified Mo/HZSM-5 via alkali treatment for improved activity in methane dehydroaromatization. Fuel Process. Technol. 235, 107387. <https://doi.org/10.1016/j.fuproc.2022.107387> **(Incorporated within Chapter 3).**
2. Mishra, D., Modak, A., Pant, K.K., Zhao, X.S., 2022b. Improved benzene selectivity for methane dehydroaromatization via modifying the zeolitic pores by dual-templating approach. Microporous Mesoporous Mater. 344, 112172. <https://doi.org/10.1016/j.micromeso.2022.112172>. **(Incorporated within Chapter 4).**
3. Mishra, D., Balyan, S., Zhao, X.S., Konarova, M., Pant, K.K., 2023a. Microwave-assisted impregnation of highly dispersed Mo over HZSM-5 using various Mo precursors for methane dehydroaromatization. React. Chem. Eng. 28–30. <https://doi.org/10.1039/D3RE00143A> with permission from the Royal Society of Chemistry. **(Incorporated within Chapter 5)**
4. Mishra, D., Modak, A., Pant, K.K., Ambeth, P.V., Konarova, M., Zhao, X.S., 2023b. Catalytic conversion of methane into benzene over ceria–zirconia-promoted molybdenum-supported zeolite for methane dehydroaromatization. Appl. Organomet. Chem. 37, e7101. <https://doi.org/10.1002/aoc.7101> **(Incorporated within Chapter 7)**

Submitted manuscripts included in this thesis

I have no other manuscripts from the thesis submitted and under review at the time of submission

Contributions by others to the thesis

In the above-listed publications, my contribution to the authored works is specified by the order of author names. For papers included in this thesis, where I appeared as a first author, I was accountable for material synthesis, testing, experiments design and implementation, data analysis, drafting of the manuscript, and preparation of figures and tables. In papers 1 and 2, Dr Sourabh Mishra helped me in setting up the test platform while Dr Arindam Modak assisted me in papers 1, 2, and 3 in writing/revising the final version of my manuscript. Dr. Sonit Balyan in Paper 4 provided me the insight on how to conduct experiments and helped me in revising the manuscript. For other sections of the papers, the corresponding authors Prof. K. K. Pant, Prof. Xiu Song (George) Zhao and Dr. Muxina Konarova guided conception and manuscript drafting. Prof. K. K. Pant, and Prof. Xiu Song (George) Zhao were responsible for securing research funds that supported the experimental consumables and

measuring instruments.

Other publications during candidature

A. Ramteke, D. Mishra, S. Mishra, K.K. Pant, D. Bhatia, Conversion of Fly-Ash into pristine ZSM-5 and its application for Methane dehydration reaction (Published)

Statement of parts of the thesis submitted to qualify for the award of another degree.

No works submitted towards another degree have been included in this thesis.

Research involving human or animal subjects.

No animal or human subjects were involved in this research.

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Mo/HZSM-5, bifunctional catalyst, hierarchical pores, acidity, Mo dispersion, Ag addition, ceria-zirconia, methane dehydroaromatization,

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ACRONYMS

Å	Angstrom
Atm	Atmosphere
Bcm	Billion cubic meters
Tcf	Trillion cubic feet
BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
XRD	X-ray diffraction
FT-IR	Fourier Transform Infrared Spectroscopy
s	Second
h	Hour
GHSV	Gas hourly space velocity
GGA	Generalized gradient approximation.
FWHM	Full width at half maximum
PW91	Perdew and Wang 91
JCPDS	Joint Committee on Powder Diffraction Standards
MDA	Methane dehydroaromatization
SAR	Silica to alumina ratio
ZSM-5	Zeolite socony mobil-5
Nm	Nanometer
UV-vis DRS	Ultra-violet Visible diffuse reflectance spectra
PSD	Particle size distribution
MFI	Framework code (IZA-International zeolite association)
SAXS	Small-angle X-ray scattering
SEM	Scanning electron spectroscopy
HAADF-STEM	High-angle annular dark field-scanning transmission electron microscopy
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