

**TOLUENE METHYLATION TO P-XYLENE:  
DEVELOPMENT OF SHAPE-SELECTIVE CATALYST  
AND KINETIC MODELLING**

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# **Toluene Methylation to p-Xylene: Development of Shape-Selective Catalyst and Kinetic Modelling**

*by*

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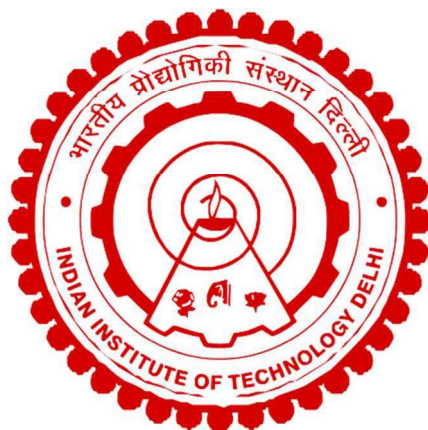
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*To my inspiring parents  
loving wife and daughter*

## Certificate

This is to certify that the thesis entitled “**Toluene Methylation to p-Xylene: Development of Shape-Selective Catalyst and Kinetic Modelling**” submitted by **Mr. Lalit Kumar** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** is a record of bonafide research work carried out by him. Mr. Lalit Kumar worked under our guidance and supervision and has fulfilled the requirements, which to our knowledge has reached the requisite standard for the submission of this thesis. The results contained in this thesis are original and have not been submitted, partially or completely, to any other University or Institute for the award of any other degree or diploma.



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*Research is to see what everybody else has seen, and to think what nobody else has thought*

Albert Szent-Györgyi

## Abstract

Owing to their narrow pore structure, ZSM-5 zeolites are widely explored for shape-selective toluene methylation to p-xylene, however, only limited success could be obtained due to two prominent reasons i.e., presence of large cavities at the intersection of microporous channels and high acid strength nature of ZSM-5 zeolites. This offset p-xylene shape selectivity advantage of these zeolites, led to undesirable side reactions and fast catalyst deactivation. Catalytic modifications e.g. reduction in pore sizes, lowering acidity, and introduction of mesopores often resulted in a trade-off between p-xylene selectivity and toluene conversion. Considering the above challenges with conventional ZSM-5 zeolites, low to moderate acid strength ZSM-48 zeolites with pores narrower than ZSM-5, absence of large cavities, and shortened crystallite sizes hypothesized as suitable to maximize toluene methylation to p-xylene.

Given above, HZSM-48 zeolite with nanoscale crystallite size was synthesized by employing multiple structure directing agents and further subjected to detailed material characterization and evaluation for the first time for toluene methylation to p-xylene. Toluene methylation activity test for prepared ZSM-48 zeolite performed in a fixed bed micro-reactor unit. Results revealed at par or higher toluene conversion (40-42 %) with a 20 % increase in p-xylene selectivity compared to conventional HZSM-5 zeolites at 400-450 °C reaction temperatures. Further, no activity loss of catalyst was reported over 72 hours time-on-stream (TOS) study, demonstrating the successful application of nano-size ZSM-48 zeolite for toluene methylation to p-xylene.

Further ZSM-48 zeolites with different silicon-to-aluminum (Si/Al) molar ratios were synthesized and the role of their acid site density was investigated for maximization of p-xylene in toluene methylation reaction. While acid strength and presence of extra-framework aluminum for synthesized ZSM-48 zeolites were determined respectively using NH<sub>3</sub>-TPD and <sup>27</sup>Al MAS NMR techniques, concentrations of Brønsted and Lewis acidic sites were measured using Pyridine-FTIR. While NH<sub>3</sub>-TPD analysis revealed the presence of only low to moderate acid strength acidic sites, <sup>27</sup>-Al MAS NMR spectroscopy confirmed the absence of extra-framework aluminum and, therefore, associated Lewis acidity and pyridine-FTIR revealed Brønsted acidic sites as prominent catalytically active sites. While low density of acid sites led to high p-xylene selectivity (42-43 %) at low toluene conversions (35-42 %), high density of acid sites resulted in low p-xylene selectivity (28-29 %) at high toluene conversions (52-55 %) in the temperature range of 375-420 °C. Low p-

xylene selectivity and high toluene conversion at high acid sites density attributed respectively to p-xylene isomerization to its two isomers o, m-xylenes at external acidic sites and highly promoted shape-selective toluene methylation to p-xylene inside narrow pores of ZSM-48 zeolite. The study suggested a combination of high acid site density interior to ZSM-48 pores along with the elimination of external acidic sites as an ideal design strategy to maximize p-xylene formation.

Further, a kinetic model for toluene methylation with methanol over ZSM-48 zeolite was developed for the first time. Based on product distribution, prominent reactions were identified. While the Eley-Rideal (ER) mechanism was used to develop kinetic expressions for toluene methylation to xylenes, simple power law models were used for other reactions. Intrinsic kinetic data free from any mass transfer limitations generated at three different temperatures 375 °C, 400 °C and 420 °C for toluene to methanol molar ratio 2 and at weight hourly space velocities (WHSV) in the range of 5-13 hr<sup>-1</sup> using a fixed bed micro-reactor unit. Developed kinetic models were fitted to the generated kinetic data. A reasonably good fit of the model to the kinetic data proved the efficacy of kinetic model equations. Employed ZSM-48 showed a lower activation energy ~ 33 kJ/mol for toluene methylation to p-xylene and 53-56 kJ/mol for toluene methylation to o, m-xylenes compared to 50-90 kJ/mol reported in the literature. The high activation energy for methanol dehydration to gaseous hydrocarbons (~ 190 kJ/mol) supported the literature findings which considered this reaction insignificant. Further methanol adsorption energy was estimated to be -129 kJ/mol which was found to be of the order of -118 to -130 kJ/mol reported for ZSM-5 zeolites.

Finally, to validate and demonstrate the design strategy for highly p-xylene selective ZSM-48 zeolite, a high acid site density ZSM-48 (Si/Al: 60) zeolite was synthesized and further silylated using chemical liquid deposition (CLD) technique by employing tetraethylorthosilicate (TEOS) as a silylating agent to cap its external acidic sites. A SiO<sub>2</sub> loading of 6.5 % (w/w) resulted in a 14-21 % increase in p-xylene selectivity compared to un-silylated parent ZSM-48 zeolite in the temperature range of 375-450 °C. Further, an increase in methylation temperature from 375 °C to 450 °C led to an increase in p-xylene selectivity from 38 to 47 % and toluene conversion from 44 to 58 % for silylated ZSM-48 zeolite which validated the efficacy of the proposed ZSM-48 design strategy. Thus, a combination of nano crystallite size, narrow pore and low to moderate acid strength along with silylation of external acidic sites opened a new window for designing of highly p-xylene selective ZSM-48 zeolite catalyst for toluene methylation to p-xylene.

## सार

माइक्रोपोरस संकीर्ण छिद्र संरचना के कारण, जेडएसएम -5 जिओलाइट्स उत्प्रेरकों को आकार-चयनात्मक टोल्यानि मिथाइलेशन अभिक्रिया से पैरा-ज़ाइलीन बनाने के लिए के लिए पारंपरिक तौर पर व्यापक रूप से उपयोग किया गया है , लेकिन, दो प्रमुख कारणों जैसे कि उनके माइक्रोपोरस चैनलों के प्रतिच्छेदन पर बड़ी गुहाओं की उपस्थिति और उनकी उच्च अम्ल क्षमता प्रकृति से केवल सीमित सफलता ही प्राप्त की जा सकी है क्योंकि इन कारणों ने न केवल इन जिओलाइट्स के पैरा-ज़ाइलीन के आकार चयनात्मकता लाभ को निरस्त किया बल्कि अवांछनीय पक्ष अभिक्रियाओं और जेडएसएम -5 उत्प्रेरक की शीघ्र निष्क्रियता को प्रोत्साहित किया . जेडएसएम -5 उत्प्रेरक संशोधन जैसे माइक्रोपोरस संकीर्ण छिद्र के आकार को कम करना, उनकी अम्लता को कम करना, और उनकी माइक्रोपोरस संकीर्ण छिद्र संरचना में मेसोपोर्स को बनाने के परिणामस्वरूप अक्सर पैरा-ज़ाइलीन चयनात्मकता और टोल्यानि रूपांतरण के बीच एक असामंजस्य देखा गया । पारंपरिक जेडएसएम -5 जिओलाइट्स के साथ उपरोक्त चुनौतियों को ध्यान में रखते हुए, मध्यम अम्ल क्षमता और छोटे क्रिस्टलीय आकारों वाले जेडएसएम -48 जिओलाइट्स को उनके जेडएसएम -5 जिओलाइट्स से ज्यादा संकीर्ण छिद्रों एवं बड़े गुहाओं की अनुपस्थिति के कारण पैरा-ज़ाइलीन को टोल्यानि मिथाइलेशन अभिक्रिया में अधिकतम करने के लिए उपयुक्त माना गया, जिसे आगे उष्मागतिकी जांच द्वारा मान्य किया गया जिसने उपर्युक्त मान्यता को और अधिक बल दिया !

प्रस्तुत अनुसंधान कार्य में, जेडएसएम -48 जिओलाइट को कई संरचना निर्देशन एजेंटों को नियोजित करके नैनोस्केल क्रिस्टलीय आकार के साथ संश्लेषित किया गया है और आगे उनका विस्तृत गुण निरूपण एवं टोल्यानि मिथाइलेशन अभिक्रिया से पैरा-ज़ाइलीन बनाने के लिए पहली बार मूल्यांकन किया गया है। संश्लेषित जेडएसएम -48 जिओलाइट के लिए टोल्यानि मिथाइलेशन अभिक्रिया परीक्षण एक माइक्रो-रिएक्टर इकाई में किया गया। 400-450 डिग्री सेल्सियस प्रतिक्रिया तापमान पर पारंपरिक एचजेडएसएम -5 जिओलाइट्स की तुलना में जेडएसएम -48 जिओलाइट के लिए पैरा-ज़ाइलीन चयनात्मकता में 20% की वृद्धि के साथ 40-42% उच्च टोल्यानि रूपांतरण के परिणाम सामने आए। इसके अलावा, 72 घंटे के समय के निरंतर गतिविधि जांच में जेडएसएम -48 जिओलाइट उत्प्रेरक की गतिविधि में किसी भी प्रकार की हानि नहीं देखी गई, जो टोल्यानि मिथाइलेशन से पैरा-ज़ाइलीन बनाने के लिए नैनो-आकार जेडएसएम -48 जिओलाइट के सफल अनुप्रयोग का प्रदर्शन करता है।

इसके अलावा प्रस्तुत कार्य में विभिन्न सिलिकॉन-टू-एल्यूमीनियम (Si/Al) अनुपात वाले जेडएसएम -48 जिओलाइट्स को संश्लेषित किया गया और टोल्यानि मिथाइलेशन अभिक्रिया में पैरा-ज़ाइलीन के अधिकतमकरण के लिए उनके अम्ल केंद्र घनत्व की भूमिका की जांच की गई । जबकि अम्ल-क्षमता और संश्लेषित जेडएसएम -48 जिओलाइट्स

के अतिरिक्त ढांचे में एल्यूमीनियम की उपस्थिति क्रमशः अमोनिया-टीपीडी और 27 अल मास एनएमआर तकनीकों का उपयोग करके निर्धारित की गई। ब्रोस्टेड और लुईस अम्लीय केन्द्रों की सांद्रता को पाइरीडीन-एफटीआईआर का उपयोग करके मापा गया। अमोनिया-टीपीडी विश्लेषण ने केवल कम से मध्यम अम्ल क्षमता वाले अम्लीय केन्द्रों की उपस्थिति का खुलासा किया, 27-अल एमएस एनएमआर स्पेक्ट्रोस्कोपी ने अतिरिक्त-ढांचे में एल्यूमीनियम और इसलिए लूइस अम्लीय साइटों की अनुपस्थिति की पुष्टि की जबकि पाइरीडीन-एफटीआईआर ने ब्रोस्टेड अम्लीय साइटों को प्रमुख उत्प्रेरक सक्रिय साइटों के रूप में प्रकट किया। कम अम्ल केंद्र घनत्व वाले एचज़ेडएसएम-48 उत्प्रेरकों ने कम टोल्यूनि रूपांतरणों (42-43%) के साथ उच्च पैरा-ज़ाइलीन चयनात्मकता (35-42%) के परिणाम दिये जबकि उच्च घनत्व वाले एचज़ेडएसएम-48 उत्प्रेरकों ने उच्च टोल्यूनि रूपांतरणों (52-55%) के साथ कम पैरा-ज़ाइलीन चयनात्मकता (28-29%) के परिणाम दिये।

इसके अलावा, जेडएसएम-48 जिओलाइट उत्प्रेरक का उपयोग करके मेथनॉल के साथ टोल्यूनि मिथाइलेशन के लिए एक काइनेटिक मॉडल पहली बार विकसित किया गया। उत्पाद वितरण के आधार पर, प्रमुख अभिक्रियाओं की पहचान की गई। एली-रिडियल मॉडल का उपयोग टोल्यूनि मिथाइलेशन से जाइलीन अभिक्रियाओं के लिए काइनेटिक अभिव्यक्तियों को विकसित करने के लिए किया गया, जबकि अन्य अभिक्रियाओं के लिए सरल काइनेटिक मॉडल का उपयोग किया गया। डब्ल्यूएचएसवी 5-13/घंटा की सीमा में टोल्यूनि मेथनॉल अनुपात 2 के लिए तीन अलग-अलग तापमानों 375 डिग्री सेल्सियस, 400 डिग्री सेल्सियस और 420 डिग्री सेल्सियस पर द्रव्यमान स्थानांतरण सीमाओं से मुक्त गतिज डेटा माइक्रो-रिएक्टर इकाई का उपयोग करके उत्पन्न किया गया एवं विकसित गतिज मॉडल उत्पन्न गतिज डेटा में फिट किए गए। काइनेटिक डेटा के लिए मॉडल का एक अच्छे फिट ने काइनेटिक मॉडल समीकरणों की प्रभावकारिता को साबित किया। नियोजित एचज़ेडएसएम-48 के लिए टोल्यूनि मिथाइलेशन से पैरा-ज़ाइलीन अभिक्रिया की सक्रियण ऊर्जा ~ 33 किलोजूल/मोल प्राप्त हुई जोकि टोल्यूनि मिथाइलेशन के साहित्य में रिपोर्ट की गई पैरा-ज़ाइलीन बनाने के लिए सक्रियण ऊर्जा 53-56 किलोजूल/मोल एवं ओरथों, मेटा-ज़ाइलीन के लिए सक्रियण ऊर्जा 50-90 किलोजूल/मोल की तुलना में कम सिद्ध हुई। मेथनॉल निर्जलीकरण से गैसीय हाइड्रोकार्बन अभिक्रिया के लिए उच्च सक्रियण ऊर्जा (~ 190 किलोजूल/मोल) ने साहित्य निष्कर्षों का समर्थन किया जो इस अभिक्रिया को महत्वहीन मानते थे। इसके अलावा, विकसित काइनेटिक मॉडल से मेथनॉल अधिशोषण ऊर्जा -129 kJ/mol होने का अनुमान लगाया गया जो जेडएसएम-5 जिओलाइट्स के लिए -118 से -130 किलोजूल/मोल के क्रम का पाया गया।

अंत में, अधिक से अधिक पैरा-ज़ाइलीन चयनात्मक एचज़ेडएसएम-48 जिओलाइट की अभिकल्पना रणनीति को मान्य और प्रदर्शित करने के लिए, एक उच्च अम्ल केंद्र घनत्व एचज़ेडएसएम-48 (Si/Al: 60) जिओलाइट को संश्लेषित किया गया और रासायनिक तरल जमाव (CLD) तकनीक का उपयोग करके टेट्राएथिलऑर्थोसिलिकेट

(TEOS) को जेडएसएम -48 जिओलाइट के बाहरी अम्लीय केंद्रों का आच्छदन करने के लिए एक सिलिलेटिंग एजेंट के रूप में नियोजित किया गया। 6.5 प्रतिशत (भार/भार) की सिलिका लोडिंग के परिणामस्वरूप 375-450 डिग्री सेल्सियस की तापमान सीमा में अन-सिलिलेटेड पैरेंट ज़ेडएसएम-48 जिओलाइट की तुलना में सिलिलेटेड ज़ेडएसएम-48 जिओलाइट के लिए पैरा-ज़ाइलीन चयनात्मकता में 14-21% की वृद्धि हुई। इसके अलावा सिलिलेटेड जेडएसएम -48 जिओलाइट के लिए, 375 डिग्री सेल्सियस से 450 डिग्री सेल्सियस तक मिथाइलेशन तापमान में वृद्धि करने से पैरा-ज़ाइलीन चयनात्मकता में 38 से 47% और टोल्यूनि रूपांतरण में 44 से 58% तक वृद्धि हुई, जिसने प्रस्तावित जेडएसएम -48 की रचना रणनीति की प्रभावकारिता को मान्य किया। इस प्रकार, नैनो क्रिस्टलीय आकार, संकीर्ण छिद्र और बाहरी अम्लीय केंद्रों के सिलिलेशन के साथ मध्यम अम्ल क्षमता के संयोजन ने अत्यधिक पैरा-ज़ाइलीन चयनात्मक वाले जेडएसएम -48 जिओलाइट की अभिकल्पना के लिए एक नई दिशा खोली।

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# Nomenclature

$A_B$	Area under Brønsted acidic sites peak in pyridine FTIR
$A_L$	Area under Lewis acidic sites peak in pyridine FTIR
$a_i$	Constants relating specific heat for species 'i' to temperature
B/L	Ratio of Brønsted and Lewis acidic sites
$b_i$	Constants relating specific heat for species 'i' to temperature
$C_{Pi}$	Heat capacity for species 'i'
$\Delta C_P$	Specific heat capacity change
$c_i$	Constants relating specific heat for species 'i' to temperature
$C_0$	Total concentration of acidic/adsorption sites
D	Crystallite size
d	d-spacing (interplanar distance)
$\Delta G_R$	Gibbs free energy change of reaction
$\Delta G^0$	Standard Gibbs free energy change of reaction
$\Delta H_R$	Heat of reaction
$H_f^0$	Standard heat of formation
$\Delta H_R^0$	Standard heat of reaction
$H_{f,i}^0$	Standard heat of formation for species 'i'
$K_{eq}$	Equilibrium constant
K	Kelvin
k	Shape constant
K1	Equilibrium for methanol adsorption
K2A	Equilibrium constant for p-xylene formation at surface
K2B	Equilibrium constant for m-xylene formation at surface.
K2C	Equilibrium constant for o-xylene formation at surface

K3A	Equilibrium constant for p-xylene desorption
K3B	Equilibrium constant for m-xylene desorption
K3C	Equilibrium constant for o-xylene desorption
$k_{1f}$	Forward rate constant: methanol adsorption reaction
$k_{1b}$	Backward rate constant: methanol adsorption reaction
$k_{2Af}$	Forward rate constant: toluene methylation to p-xylene
$k_{2Ab}$	Backward rate constant: toluene methylation to p-xylene
$k_{2Bf}$	Forward rate constant: toluene methylation to m-xylene
$k_{2Bb}$	Backward rate constant: toluene methylation to m-xylene
$k_{3Cf}$	Forward rate constant: toluene methylation to o-xylene
$k_{3Cb}$	Backward rate constant: toluene methylation to o-xylene
$N_B$	Brønsted acidic sites concentration
$N_L$	Lewis acidic sites concentration
n	Integer
R	Gas constant (joule/mol °K)
S	Cross-section of wafer (m <sup>2</sup> )
$S_{BET}$	Total surface area (m <sup>2</sup> /g)
$S_{micro}$	Micropore surface area (m <sup>2</sup> /g)
$S^0$	Standard entropy
$S_i^0$	Standard entropy for species 'i'
$S^*$	Concentration of vacant adsorption sites
$\Delta S_R$	Entropy change of reaction
$\Delta S_R^0$	Standard entropy change of reaction
T	Temperature

$T_0$	Standard temperature
$V_{\text{micro}}$	Micropore volume ( $\text{m}^3/\text{g}$ )
$V_{\text{meso+macro}}$	Meso and macropore volume ( $\text{m}^3/\text{g}$ )
$X_{\text{MeOH}}$	Methanol conversion
$X_{\text{T}}$	Toluene conversion

### **Greek Letters**

$\theta$	X-ray scattered angle
$\beta$	Full width at half maximum
$\lambda$	Wavelength ( $\text{\AA}$ )
$\nu_i$	Stoichiometry coefficient
$\varepsilon_{\text{B}}$	Molar extinction coefficient for Brønsted acidic sites
$\varepsilon_{\text{L}}$	Molar extinction coefficient for Lewis acidic sites

### **Subscripts**

$i$	Index used for referring components
$j$	Index used for referring sign of stoichiometric coefficient