

**MODULATING ACTIVE SITES TO DECIPHER PRIMARY
CARBON SOURCE FOR METHANOL AND DIMETHYL
ETHER SYNTHESIS FROM COAL/BIOMASS DERIVED CO₂
RICH SYNGAS *VIA* TANDEM CATALYSIS**

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INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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by

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Department of Chemical Engineering

Submitted

in fulfilment of the requirements for the degree of Doctor of Philosophy

to the



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Dedicated to my parents

Arvind Kumar Tripathi and Krishna Tripathi

Without whom this journey would have been incomplete

CERTIFICATE

This is to certify that the thesis titled “**Modulating active sites to decipher primary carbon source for methanol and dimethyl ether synthesis from coal/biomass derived CO₂ rich syngas via tandem catalysis**” being submitted by **Ms. Komal Tripathi** 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 her. **Ms. Komal Tripathi** 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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Abstract

The ever rising demand for energy and dwindling crude oil reserves has prioritized the need for non-crude oil based energy systems such as coal, pet coke and biomass. Since coal is one of the most abundant and evenly distributed fossil fuel, thus searching for clean coal conversion technologies is the current need of hour. The syngas derived from coal and biomass gasification comprises a significant fraction of CO₂ (3-15%) along with CO, resulting in CO₂-rich and H₂-deficient feed gas. The direct chemical transformation of this CO₂ rich syngas into methanol/dimethyl ether (DME) gives a distinct edge to this methodology amongst different “CO₂ valorisation” techniques. The conventional Cu-based catalytic system for methanol/DME synthesis is highly optimized for syngas feed having CO₂ only up to 3 vol%. However, the process for utilizing CO₂ rich streams (having up to 30% CO₂) is relatively less developed. Moreover, Cu based catalysts generally suffer from poor stability under industrial reaction conditions. Although it is believed that Cu⁰ active sites contributes to catalytic activity for conventional syngas, but the exact nature and mechanistic aspects of active sites (Cu⁰ or Cu⁺ or Cu⁰/Cu⁺) is under debate for CO₂ rich syngas. Furthermore, there is also a debate on the primary carbon source for methanol/DME synthesis and the origin of evolution of different types of Cu species. Therefore, rational design of Cu-based catalysts for CO₂ rich syngas was formulated via addition of bivalent/trivalent cation promoters of reducible-nonreducible nature.

In view of this, initially comprehensive thermodynamic study in adiabatic and isothermal processes was conducted to evaluate the comparative efficacy of methanol and DME synthesis using wide range of reaction parameters: reaction temperature (180 °C-280 °C), reaction pressure (10-80 bar), SN number (0-11), CO₂/(CO₂+CO) molar feed ratio (0-1). Based on the equilibrium yield, one-step DME synthesis was discovered as the most viable process to utilize the coal/biomass derived syngas effectively. Further, the overall process efficiency was inspected through the process design of 1 TPD DME plant resulting in significant CO₂ abatement and DME production with high product purity and minimum energy consumption.

To gain experimental insights of the process, a series of Mn promoted highly substituted malachite precursors were synthesized by varying Mn loading and applied for methanol synthesis reaction. The same precursor materials were also employed for DME synthesis reaction using tandem catalysis approach. For this, bifunctional catalytic sites were introduced using γ -Al₂O₃ as a methanol dehydrating agent along with these precursors. The structural changes within the catalytic entity were analyzed as a function of MnO content. Investigations revealed that incorporating 20 mol% Mn in precursor phase (malachite lattice) resulted in better

stabilization and dispersion of CuO domains as compared to other analogous catalysts. This is due to maximum dilution of Cu²⁺ ions since MnO has similar charge as Zn²⁺ and only 4% less ionic radii relative to Cu²⁺. Consequently, this catalyst resulted in ~1.4-fold and ~1.2-fold increase in CO conversion ($X_{\text{CO}} = 46\%$) and methanol selectivity ($S_{\text{CH}_3\text{OH}} = 93\%$) at respectively as compared to the unpromoted catalyst. Interestingly, same catalyst with bifunctional sites also demonstrated an ~2.7 and ~1.8-fold increase in total carbon conversion ($X_{\text{CO}+\text{CO}_2} = 36.2\%$) and DME selectivity ($S_{\text{DME}} = 73.8\%$) relative to unpromoted one. It was also gathered that the surface Cu⁺/Cu⁰ ratio was regulated at reaction conditions by optimizing MnO composition. This is probably due to stabilization of the active centers for methanol/DME formation. The resulting co-existence of stabilized dual active sites (Cu⁰ and Cu⁺) validate both formate and rWGS CO-hydro pathways for hybrid feed hydrogenation and provides insights for carbon source from which methanol/DME originates.

Apart from these findings, identification of most suitable precursor phase for synthesis is still debatable. Accordingly, a series of La-promoted Cu/ZnO/MgO catalysts were synthesized to understand the evolution of stable phase mixed precursors. The optimized catalyst (2.5 mol% La) demonstrated the amplified population of malachite phase and a suppression in aurichalcite phase. Presence of mixed phase precursor reflected well in Cu dispersion, small sized stable Cu particles and improved methanol synthesis activity with marginal deterioration in activity over 60 h on stream. CZ-M_{17.5}La_{2.5} catalyst showed the highest carbon conversion with a methanol selectivity of 72.2% at 260 °C.

All above results revealed the complexity of interplay of activity results with synthesis and reaction conditions due to the structure sensitive nature of the reaction. An ultra-fast machine learning (ML) based framework was therefore developed using extensive database construction from existing published literature to uncover catalytic property-performance correlations hidden in large body of existing experimental research. Overall through these systematic studies, the dissertation provides insights of active surface sites, primary carbon source, origin of different types of Cu sites for the reaction. Nonetheless, this study also gives insights underlying precursor phase chemistry and guide a way to future catalyst design. To summarize, the formulated coal to methanol/DME route paves the way for sustainable solutions referring to global “3E” issues, viz. energy, environment, and economic challenges.

सारांश

ऊर्जा की लगातार बढ़ती मांग और घटते कच्चे तेल के भंडार ने गैर-कच्चे तेल पर आधारित ऊर्जा प्रणालियों जैसे कोयला, पेट कोक और बायोमास की आवश्यकता को प्राथमिकता दी है। चूंकि कोयला सबसे प्रचुर मात्रा में और समान रूप से वितरित जीवाश्म ईंधन में से एक है, इस प्रकार स्वच्छ कोयला रूपांतरण की खोज और प्रौद्योगिकियां वर्तमान समय की आवश्यकता है। CO_2 -समृद्ध और H_2 -न्यून फ्रीड गैस के परिणामस्वरूप, कोयले और बायोमास गैसीकरण से प्राप्त सिनगैस में CO के साथ CO_2 (3-15%) का एक महत्वपूर्ण अंश शामिल है। इस CO_2 समृद्ध सिनगैस का प्रत्यक्ष रासायनिक रूपांतरण मेथनॉल/डाइमिथाइल ईथर (डीएमई), " CO_2 वैलोरिसेशन" तकनीक पद्धति को विभिन्न तरीकों के बीच एक अलग बढ़त देता है। 3 वोल्ट% तक CO_2 वाले सिनगैस फ्रीड के लिए, मेथनॉल/डीएमई के संश्लेषण की पारंपरिक Cu -आधारित उत्प्रेरक प्रणाली अत्यधिक अनुकूलित है। हालांकि CO_2 समृद्ध धाराओं (30% CO_2 तक) के उपयोग की प्रक्रिया अपेक्षाकृत कम विकसित है। इसके अलावा, Cu आधारित उत्प्रेरक आमतौर पर औद्योगिक प्रतिक्रिया स्थिति के तहत अच्छी स्थिरता नहीं रखते हैं। हालांकि यह माना जाता है कि Cu^0 सक्रिय स्थल पारंपरिक सिनगैस उत्प्रेरक गतिविधि में योगदान करते हैं, लेकिन CO_2 समृद्ध सिनगैस के लिए सक्रिय साइटों की सटीक प्रकृति और यंत्रणत पहलू (Cu^0 या Cu^+ या Cu^0/Cu^+) बहस का मुद्दा है। इसके अलावा, मेथनॉल/डीएमई संश्लेषण के लिए प्राथमिक कार्बन स्रोत और विभिन्न विकास की Cu प्रजातियों के प्रकार की उत्पत्ति पर भी बहस चल रही है। इसलिए, रिड्यूसिबल-नॉनरेड्यूसिबल नेचर के बाइवैलेंट/ट्रिवैलेंट केशन प्रमोटर्स को जोड़कर, CO_2 समृद्ध सिनगैस के लिए Cu -आधारित उत्प्रेरकों का तर्कसंगत डिजाइन तैयार किया गया।

इसे देखते हुए, मेथनॉल और डीएमई संश्लेषण की तुलनात्मक प्रभावकारिता का मूल्यांकन करने के लिए, रूद्धोष्म और समतापीय प्रक्रिया में प्रारंभिक रूप से व्यापक ऊष्मप्रवैगिकी अध्ययन प्रक्रियाएं पूर्ण की गईं जिसमें प्रतिक्रिया मापदंडों की विस्तृत श्रृंखला: प्रतिक्रिया तापमान (180 °C-280 °C), प्रतिक्रिया दबाव (10-80 बार), SN नंबर (0-11), $\text{CO}_2/(\text{CO}_2+\text{CO})$ मोलर फ्रीड अनुपात (0-1) शामिल है। साम्यवस्था उपज पर आधारित, कोयला/बायोमास व्युत्पन्न सिनगैस को प्रभावी ढंग से उपयोग करने के लिए एक-चरण वाला डीएमई संश्लेषण सबसे व्यवहार्य प्रक्रिया के रूप में खोजा गया। इसके अलावा 1 टीपीडी डीएमई संयंत्र की प्रक्रिया डिजाइन के माध्यम से, समग्र प्रक्रिया की दक्षता का निरीक्षण किया गया जिसके परिणामस्वरूप उच्च उत्पाद शुद्धता और न्यूनतम ऊर्जा खपत के साथ कमी के साथ डीएमई और CO_2 का उत्पादन हुआ। प्रक्रिया की प्रायोगिक अंतर्दृष्टि प्राप्त करने के लिए, मैलाकाइट अग्रदूतों को विभिन्न Mn लोडिंग करके, Mn की एक श्रृंखला को अत्यधिक प्रतिस्थापित किया गया जिससे मेथनॉल संश्लेषित किया गया। अग्रानुक्रम कटैलिसिस दृष्टिकोण का उपयोग कर, DME संश्लेषण के लिए समान अग्रदूत सामग्री भी नियोजित की गई। इसके लिए बाइफंक्शनल कैटैलिटिक साइट्स को इन अग्रदूतों के साथ मेथनॉल डिहाइड्रेटिंग एजेंट के रूप में $\gamma\text{-Al}_2\text{O}_3$ का उपयोग करके पैदा की गई। MnO सामग्री के रूप में, उत्प्रेरक इकाई के भीतर संरचनात्मक परिवर्तन का विश्लेषण किया गया।

जांच के आधार पर पता चला कि अग्रदूत चरण (मैलाकाइट जाली) में 20 mol% Mn को शामिल करने से स्थिरीकरण और CuO डोमेन के फैलाव में अन्य समान उत्प्रेरकों की तुलना में बेहतर परिणाम मिले। यह Cu^{2+} आयनों के अधिकतम तनुकरण के कारण है क्योंकि MnO पर Zn^{2+} के समान आवेश होता है और केवल 4% कम Cu^{2+} के सापेक्ष आयनिक त्रिज्या होती है। नतीजतन, अप्रमाणित उत्प्रेरक की तुलना में, इस उत्प्रेरक का CO रूपांतरण में वृद्धि ($X_{\text{CO}} = 46\%$) और मेथनॉल चयनात्मकता ($S_{\text{CH}_3\text{OH}} = 93\%$) में परिणाम क्रमशः लगभग 1.4-गुना और 1.2-गुना पाया गया। दिलचस्प है, एक ही उत्प्रेरक ने द्विकार्यात्मक साइटों के साथ भी कुल कार्बन रूपांतरण में ~ 2.7 और ~ 1.8 गुना वृद्धि ($X_{\text{CO}+\text{CO}_2} = 36.2\%$) और अप्रमाणित के सापेक्ष DME चयनात्मकता ($S_{\text{DME}} = 73.8\%$) का प्रदर्शन किया। परिणामों से यह भी पता चला कि इष्टतम MnO सामग्री Cu^+/Cu^0 सतह को सटीक रूप से ट्यून करती है, तथा इसी प्रकार लागू प्रतिक्रिया के तहत मेथनॉल/डीएमई गठन के लिए सक्रिय केंद्रों को स्थिर करती है। स्थिर दोहरी सक्रिय साइटों का परिणामी सह-अस्तित्व (Cu^0 और Cu^+) हाइब्रिड फीड हाइड्रोजनीकरण के लिए दोनों फॉर्मेट और rWGS CO-हाइड्रो पाथवे प्रदान करता है और कार्बन स्रोत के लिए अंतर्दृष्टि प्रदान करता है जिससे मेथनॉल/डीएमई उत्पन्न होता है।

इन निष्कर्षों के अलावा, संश्लेषण के लिए सबसे उपयुक्त अग्रगामी चरण की पहचान अभी भी बहस योग्य है। तदनुसार, स्थिर चरण मिश्रित अग्रदूतों के विकास को समझने के लिए, La-प्रमोटेड Cu/ZnO/MgO उत्प्रेरकों की एक श्रृंखला को संश्लेषित किया गया था। अनुकूलित उत्प्रेरक (2.5 मोल% La) ने मैलाकाइट चरण की बढ़ी हुई आबादी और ऑरिकल्साइट में दमन अवस्था का प्रदर्शन किया। Cu फैलाव में, छोटे आकार के स्थिर Cu घन कणों में और स्टीम पर 60 घंटे से अधिक बेहतर मेथनॉल संश्लेषण गतिविधि में मिश्रित चरण अग्रदूत की उपस्थिति अच्छी तरह से परिलक्षित होती है। CZ-M_{17.5}La_{2.5} उत्प्रेरक ने 260 डिग्री सेल्सियस पर 72.2% की मेथनॉल चयनात्मकता के साथ उच्चतम कार्बन रूपांतरण दिखाया।

उपरोक्त सभी परिणामों ने संश्लेषण के साथ गतिविधि परिणामों के परस्पर क्रिया की जटिलता और प्रतिक्रिया की संरचना संवेदनशील प्रकृति के कारण प्रतिक्रिया की स्थिति को प्रकट किया। व्यापक डेटाबेस का उपयोग करके, उत्प्रेरक संपत्ति-प्रदर्शन सहसंबंधों को उजागर करने के लिए मौजूदा प्रकाशित साहित्य से प्रायोगिक अनुसंधान के लिए एक अल्ट्रा-फास्ट मशीन लर्निंग (एमएल) आधारित ढांचा विकसित किया गया था। कुल मिलाकर इन व्यवस्थित अध्ययन से, यह शोध अध्ययन सक्रिय सतह साइटों, प्राथमिक कार्बन स्रोत, प्रतिक्रिया के लिए विभिन्न प्रकार की Cu साइटों की उत्पत्ति की अंतर्दृष्टि प्रदान करता है। बहरहाल, यह अध्ययन अंतर्निहित अग्रदूत चरण रसायन विज्ञान और भविष्य के उत्प्रेरक डिजाइन के लिए एक मार्ग का मार्गदर्शन करता है और अंतर्दृष्टि भी देता है। संक्षेप में, वैश्विक "3E" मुद्दों के लिए अर्थात् ऊर्जा, पर्यावरण और आर्थिक चुनौतियों की चर्चा करते हुए, तैयार किए गए कोयले से मेथनॉल/डीएमई मार्ग संदर्भित करने वाले स्थायी समाधानों का मार्ग प्रशस्त करता है।

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Acronyms

DME	Dimethyl Ether
ICI	Imperial Chemical Industries
STM	Syngas to Methanol
CTM	CO ₂ /CO ₂ rich syngas to Methanol
LPLT	Low Pressure Low Temperature
HTHP	High Temperature High Pressure
SRK	Soave-Redlich-Kwong
EOS	Equation of State
XRD	X-ray Diffraction
XPS	X-ray Photoelectron Spectroscopy
AES	Auger Electron Spectroscopy
XAES	X-ray Auger Electron Spectroscopy
JCPDS	Joint Committee on Powder Diffraction Standards
FESEM	Field Emission Scanning Electron Microscopy
HRTEM	High Resolution Transmission Electron Microscope
TPR	Temperature Programmed Reduction
TCD	Thermal Conductivity Detector
TPD	Temperature Programmed Desorption
MPAES	Microwave Plasma Atomic Emission Spectroscopy
FID	Flame Ionization Detector
GC	Gas Chromatography
RSM	Response Surface Methodology
CCD	Central Composite Design
ANOVA	Analysis of Variance
Gt	Gigatonnes
WGS	Water Gas Shift
rWGS	Reverse Water Gas Shift
LHHW	Langmuir-Hinshelwood-Hougen-Watson
RDS	Rate Determining Step
STD	Syngas to DME
SN	Stoichiometric Number

COR	Carbon Oxides Ratios
MFC	Mass Flow Controllers
ML	Machine Learning
ANN	Artificial Neural Network
RMSE	Root Mean Square Error
WHSV	Weight Hourly Space Velocity
GHSV	Gas Hourly Space Velocity
TPD	Tonnes Per Day
TOS	Time on Stream