CATALYTIC CONVERSION OF CO_2 TO METHANOL OVER SUPPORTED INTERMETALLIC CATALYST

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INDIAN INSTITUTE OF TECHNOLOGY DELHI

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by

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Submitted

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CERTIFICATE

This is to certify that the thesis titled **“Catalytic conversion of CO_2 to methanol over supported intermetallic catalyst”** being submitted by **Mr. Kaisar Ahmad Hajam** 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. Kaisar Ahmad Hajam has worked under my 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 global warming and change in climatic conditions due to the rising concentration of CO_2 in the atmosphere are the most important challenges of the 21st century. Catalytic conversion of CO_2 to methanol will not only check global warming but will also provide an alternative source of fuel. In this thesis, a detailed experimental investigation into direct hydrogenation of CO_2 to methanol has been carried out. Herein, initially, a comprehensive and comparative thermodynamic analysis of various CO_2 hydrogenation processes including methanol synthesis was performed in a wide range of reaction conditions. The thermodynamic limitations of the reaction and favourable range of reaction-parameters were then found to be helpful in the experimental investigations. In the experimental work, a new class of intermetallic catalysts was prepared and tested for the CO_2 hydrogenation to methanol. The alloys of Ga with Pd and Ni over SiO_2 support were synthesized using different preparation methods to get the most desirable catalytic properties. The prepared catalysts were characterized by various techniques like XRD, TEM-EDX, SEM, BET, H_2-chemisorption, H_2-TPR, CO_2-TPD, ICP-MS, and FTIR. The activity test of the H_2-reduced catalysts was carried out in a differential plug flow fixed bed reactor. From the catalyst screening, the Ga_3Ni_5/SiO_2 catalyst prepared through the co-precipitation method was found to be most active for methanol synthesis among all the catalysts including Pd_2Ga/SiO_2. Further analysis like the influence of various reaction parameters on catalytic activity to get the best set of parameter values was performed over co-precipitated Ga_3Ni_5/SiO_2 catalyst. The co-precipitated Ga_3Ni_5/SiO_2 catalyst was found to be more active than the traditional $Cu/ZnO/Al_2O_3$ methanol catalyst under the same reaction conditions. A detailed kinetic analysis of methanol synthesis from CO_2/H_2 including RWGS reaction over Ga_3Ni_5 catalyst was performed in a continuous plug flow fixed bed reactor after identifying the mass transfer resistance-free regime. From the kinetic study, the hydrogenation of formate to give surface-bound H_2COO was found to be the rate-determining step. The kinetic model was

found to follow a single site mechanism and was found consistent with literature reports. The Ga_3Ni_5-CP (co-precipitated) also showed better stability followed by Ga_3Ni_5-IWI and Ga_3Ni_5-CE respectively. From the deactivation analysis, the loss in catalytic activity is attributed to the loss of active surface area due to sintering and Carbon-deposition as evident from the spent catalyst characterizations. The higher activity was related to the highly accessible Ga_3Ni_5 surface during methanol synthesis. From the deactivation kinetics, the deactivation rate of Ga_3Ni_5 catalysts was found to fit the first order power-law model and in the order of their deactivation constants, Ga_3Ni_5-CE > Ga_3Ni_5-IWI > Ga_3Ni_5-CP.

सार

वातावरण में कार्बन डाइऑक्साइड की बढ़ती एकाग्रता के कारण ग्लोबल वार्मिंग और जलवायु परिस्थितियों में बदलाव इक्कीसवीं सदी की सबसे महत्वपूर्ण चुनौतियां हैं। कार्बन डाइऑक्साइड से मेथनॉल के उत्प्रेरक रूपांतरण से न केवल ग्लोबल वार्मिंग की जाँच होगी, बल्कि यह ईंधन का एक वैकल्पिक स्रोत भी प्रदान करेगा। इस थीसिस में, कार्बन डाइऑक्साइड से मेथनॉल के प्रत्यक्ष हाइड्रोजनीकरण की एक विस्तृत प्रयोगात्मक जांच की गई है। यहाँ, प्रारंभ में, मेथनॉल संश्लेषण सहित विभिन्न कार्बन डाइऑक्साइड हाइड्रोजनीकरण प्रक्रियाओं का एक व्यापक और तुलनात्मक थर्मोडायनामिक विश्लेषण प्रतिक्रिया स्थितियों की एक विस्तृत श्रृंखला में किया गया था। प्रतिक्रिया और मापदंडों की अनुकूल रेंज की थर्मोडायनामिक सीमाएं तब प्रायोगिक जांच में सहायक पाई गईं। प्रायोगिक कार्य में, इंटरहेल्मिक उत्प्रेरकों का एक नया वर्ग तैयार किया गया और कार्बन डाइऑक्साइड हाइड्रोजनीकरण से मेथनॉल के लिए परीक्षण किया गया। SiO_2 समर्थन पर पीडी और नी के साथ गा की मिश्र धातुओं को सबसे वांछनीय उत्प्रेरक गुणों को प्राप्त करने के लिए विभिन्न तैयारी विधियों का उपयोग करके संश्लेषित किया गया था। तैयार किए गए उत्प्रेरकों को विभिन्न तकनीकों जैसे XRD, TEM-EDX, SEM, BET, H_2-chemisorption, H_2-TPR, CO_2-TPD, ICP-MS और FTIR की विशेषता थी। H_2- कम उत्प्रेरक की गतिविधि परीक्षण एक अंतर प्लग फ्लो फिक्स्ड बेड रिएक्टर में किया गया था। उत्प्रेरक स्क्रीनिंग से, सह-वर्षा विधि के माध्यम से तैयार Ga_3Ni_5/SiO_2 उत्प्रेरक को Pd_2Ga/SiO_2 सहित सभी उत्प्रेरकों के बीच मेथनॉल संश्लेषण के लिए सबसे अधिक सक्रिय पाया गया। आगे के विश्लेषण जैसे कि उत्प्रेरक मूल्यों पर विभिन्न प्रतिक्रिया मापदंडों के प्रभाव को पैरामीटर मानों का सर्वोत्तम सेट प्राप्त करने के लिए सह-पूर्व निर्धारित Ga_3Ni_5/SiO_2 उत्प्रेरक पर प्रदर्शन किया गया था। सह-अवक्षेपित Ga_3Ni_5/SiO_2 उत्प्रेरक समान प्रतिक्रिया स्थितियों के तहत पारंपरिक $Cu/ZnO/Al_2O_3$ मिथेनॉल उत्प्रेरक की तुलना में अधिक सक्रिय पाया गया। Ga_3Ni_5 उत्प्रेरक पर RWGS प्रतिक्रिया सहित CO_2/H_2 से मेथनॉल संश्लेषण का एक विस्तृत गतिज विश्लेषण बड़े पैमाने पर स्थानांतरण प्रतिरोध मुक्त शासन की पहचान करने के

बाद एक सतत प्लग प्रवाह तय बिस्तर रिएक्टर में किया गया था। काइनेटिक अध्ययन से, सतह-बाध्य H_2COO देने के लिए फॉर्मेट के हाइड्रोजनेशन को दर-निर्धारण कदम माना गया। गतिज मॉडल एक एकल साइट तंत्र का पालन करने के लिए पाया गया था और साहित्य रिपोर्टों के अनुरूप पाया गया था। Ga_3Ni_5-CP (सह-अवक्षेपित) ने भी बेहतर स्थिरता दिखाई, जिसके बाद क्रमशः Ga_3Ni_5-IWI और Ga_3Ni_5-CE शामिल हैं। निष्क्रिय होने के विश्लेषण से, उत्प्रेरक गतिविधि में नुकसान को सक्रिय सतह क्षेत्र के नुकसान के लिए जिम्मेदार ठहराया जाता है क्योंकि खर्च किए गए उत्प्रेरक लक्षण से स्पष्ट होने के रूप में सिंटरिंग और कार्बन-जमाव के कारण होता है। उच्च गतिविधि मेथनॉल संश्लेषण के दौरान अत्यधिक सुलभ Ga_3Ni_5 सतह से संबंधित थी। निष्क्रियता कैनेटीक्स से, Ga_3Ni_5 उत्प्रेरकों की निष्क्रियता दर पहले के आदेश पावर-लॉ मॉडल और उनके निष्क्रियकरण स्थिरांक, Ga_3Ni_5-CE> Ga_3Ni_5-IWI> Ga_3Ni_5-CP के क्रम में फिट पाई गई।

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NOMENCLATURE

C_{Ab}	concentration of CO_2 in feed gas, [$kmol.m^{-3}$]
d_p	catalyst particle size
D	dispersion at time ‘t’
D_0	initial dispersion
D_{eq}	limiting dispersion
Đ	internal diameter of the reactor
E_a	activation energy, [kJ/mol]
$F_{i,in}$	molar flow rates of the component ‘i’ for inlet, mole/hour
$F_{i,out}$	molar flow rates of the component ‘i’ for outlet, mole/hour
ΔG_{298}	standard Gibbs energy, [$kJ.mol^{-1}$]
ΔH_{298}	standard enthalpy of formation, [$kJ.mol^{-1}$]
K_{eq}	reaction equillibrium constant
k_c	mass transfer coefficient of CO_2
k_s	deactivation constant
k_i	reaction rate constant of i^{th} elementary step
K_i	equilibrium constant of i^{th} elementary step
L	catalyst bed height, [mm]
n	order of reaction
N_{W-P}	Weisz-Prater number
P	pressure of the system, [bar]
$r_{A(obs)}$	observed rate of reaction, [$mol.kg^{-1}.s^{-1}$]
R	catalyst pellet radius, [m]
S_{MeOH}	Methanol selectivity
T	temperature of the system, [^oC]
X_{CO_2}	conversion of CO_2
α	low temperature desorption peak
β	moderate temperature desorption peak
ρ_b	catalyst bed density, [kg/m^3]

ACRONYMS

BASF	Baden Aniline and Soda Factory
CCS	carbon capture and storage
CE	condensation-evaporation
CP	co-precipitation
CRC	cyclic Redundancy Checking
CRI	carbon Recycling International
DME	dimethyl ether
DMT	dimethyl terephthalate
EDS	energy Dispersive X-ray Spectroscopy
FID	flame ionization detector
FTIR	fourier transforms infrared spectroscopy
FWHM	full width at half maximum
GC	gas chromatograph
GHSV	gas hourly space velocity
GPLE	generalized power-law expression
HC	Hydrocarbons
ICI	imperial Chemical Industries
ICP-MS	inductively coupled plasma mass spectroscopy
IEA	international Energy Agency
IWI	incipient wetness impregnation
JCPDS	joint Committee on Powder Diffraction Standards
LH-HW	Langmuir Hinshelwood-Hougen Watson
MTBE	methyl tert-butyl ether
MTO	methanol-to-olefins
PSD	particle size distribution
RWGS	reverse water gas shift
SEM	scanning electron microscopy
TCD	thermal conductivity detector
TEM	transmission electron microscopy
TEOS	tetraethyl Orthosilicate
TPR	temperature-programmed reduction
TOF	turn over frequency
XRD	X-ray diffraction
XPS	X-ray Photoelectron Spectroscopy