CONVERSION OF LOW H_2/CO RATIO SYNGAS INTO LIQUID HYDROCARBON BY FISCHER TROPSCH SYNTHESIS OVER MULTIFUNCTIONAL CATALYST

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DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
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by

SONAL

DEPARTMENT OF CHEMICAL ENGINEERING

Submitted

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

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI
FEBRUARY 2018

Dedicated to my Parents
S. S. Prasad & Manju Prasad
Without whom this journey would have been incomplete

CERTIFICATE

This is to certify that the thesis titled **"Conversion of low H_2/CO ratio syngas into liquid hydrocarbon by Fischer Tropsch synthesis over multifunctional catalyst"** being submitted by **Ms**. **Sonal** 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. Sonal** 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 stoichiometric ratio H_2/CO for selective synthesis of C_{5-20} hydrocarbons by Fisher-Tropsch process is around 2 which needs development of novel catalyst system which tunes this ratio in the syngas (with lower ratio < 2.0) from various feedstock like coal, petcoke, biomass and various gasification processes. Bimetallic catalysts of Fe-Co seem to be the answer for achieving high C_{5-20} selectivity with controlled water gas shift activity. Catalysts with varying Fe to Co weight ratio (Fe/Co = 0.25, 0.5, 1) with constant metal loading (30 %) and at constant Fe to Co weight ratio (0.5) with varying metal loadings (9, 18 and 30 %) were prepared in the laboratory by co-precipitation method. These catalysts were characterized by different techniques such as BET Surface analyzer and pore size analyzer, XRD, TPD, TPR, FTIR, SEM, TEM, and TGA. Catalyst containing 10%Fe/20%Co/SiO_2 with Fe to Co ratio of 0.5 was found to be an optimum catalyst in which more than 65 % CO conversion was achieved at 220 °C, 2.0 MPa, H_2/CO ratio of 1.48, and GHSV-1200 mL/hr-gcat. Reaction parameters temperature, pressure, H_2/CO ratio and gas hourly space velocity (GHSV) were optimized to give maximum yield of the C_5 –C_{20} hydrocarbons and they were found to be 240 ℃, 2.0 MPa, 1.48 ratio and 1200 mL/gcat-h repectively for 72 % CO conversion and 50 % C_5-C_{20} selectivity. Incorporation of 0.5% rhodium on the catalyst increases the WGS activity with increased CO conversion and increased C_{5+} selectivity. Promotion with Rh metal on the bimetallic catalyst shows that the best catalyst was 0.5Rh/10%Fe/20%Co/SiO_2 for 78% CO conversion and the 53 % selectivity to C_{5-20} hydrocarbons at the optimum conditions. Rh promoted Fe-Co bimetallic catalyst showed promise when CO_2 containing syngas was used. The product distributions shifted towards lower hydrocarbons with increasing composition of CO_2. The kinetics of FTS reaction over 10%Fe/20%Co/SiO_2 catalyst seems to follow Langmuir-Hinshelwood-Hougen-Watson and Eley-Riedel mechanisms. The developed kinetic model for the rate of CO consumption based on H-assisted CO dissociation mechanism fit the data adequately. Kinetic models were also developed for the rate of product formation in which the mechanisms of chain propagation and termination were included. The model based on chain length dependent α-olefin desorption was able to predict the non-ASF behavior, mainly the decreasing α-olefin to paraffin ratios. The activation energy of methane formation (71kJ/mol) was lower than that of the other paraffins (113 kJ/mol) which is in agreement with the observed higher mole fraction of methane in the product stream.

सार

फिशेर-ट्रॉफ़्स प्रक्रिया द्वारा C_{5-20} हाइड्रोकार्बन के चयनात्मक संश्लेषण के लिए स्टोइचीओमेट्रिक हाइड्रोजन और कार्बन मोनो ऑक्सिड अनुपात की आवश्यकता लगभग 2 है, जो उत्प्रेरक प्रणाली के विकास की आवश्यकता है, कोयले, पेटकोक , बायोमास क़े विभिन्न गैसीकरण प्रक्रियाएं द्वारा यह अनुपात को SYN गैस (कम अनुपात <2.0) कम प्रप्त होत है जिसे Fe- Co के बायमेटेलिक उत्प्रेरकों का प्रयोग कर के और नियंत्रित WGS अभिक्रिया के साथ उच्च C_{5-20} चुनिंदा को प्राप्त किया जा सकता है। अलग-अलग मेटल लोडिंग (9, 18 और 30%) के साथ धातु लोडिंग (30%) और अलग-अलग सह वजन अनुपात (Fe / Co = 0.25, 0.5, 1) के अलग-अलग Fe Co उत्प्रेरक Co-precipitation विधि द्वारा प्रयोगशाला में तैयार किए गए थे। ये उत्प्रेरक विभिन्न तकनीक जैसे कि बीईटी (BET) विश्लेषक, एक्सआरडी (XRD), टीपीडी(TPD), टीपीआर (TPR), एफटीआईआर (FTIR), और टीजीए(TGA) के द्वारा विश्लेषित किये गये। 0.5 के सह-अनुपात के साथ 10% Fe / 20% Co / SiO_2 के साथ उत्प्रेरक एक इष्टतम उत्प्रेरक पाया गया जिसमें 220 ° सी, 2.0 MPa, H_2/CO अनुपात में 1.48 से अधिक 65% कार्बन मोनो ऑक्सिड रूपांतरण प्राप्त किया गया था, और GHSV-1200 एमएल प्रति घन्टा-प्रति ग्राम उत्प्रेरक रिएक्शन मापदंडों तापमान, दबाव, H_2/CO अनुपात और गैस प्रति घंटा वेग (जीएचएसवी) C_{5-20} हाइड्रोकार्बन की अधिकतम उपज देने के लिए अनुकूलित थे और वे 240 ℃, 2.0 एमपीए(मेगा पश्कल) , 1.48 अनुपात और 1200 गैस प्रति घंटा वेग 72% सीओ रूपांतरण और 50% C_{5-20} चयनात्मकता के लिए निश्चित रूप से एच। उत्प्रेरक पर 0.5% Rh का सम्मिलन WGS गतिविधि को बढ़ाता हुआ सीओ रूपांतरण और C_{5+} चयनात्मकता बढ़ाता है। द्विमितीय उत्प्रेरक पर आरएच मेटल के साथ संवर्धन दर्शाता है कि सबसे अच्छा उत्प्रेरक 78% सीओ रूपांतरण के लिए 0.5 0.5Rh/10%Fe/20%Co/SiO_2 था और इष्टतम स्थितियों में C_{5-20} हाइड्रोकार्बन की 53% चयनात्मकता। Rh ने सम्मिलन किए गए Fe- Co bimetallic उत्प्रेरक ने वादा दिखाया जब CO_2 युक्त सीएनजी इस्तेमाल किया गया था। CO_2 की बढ़ती रचना के साथ उत्पाद वितरण कम हाइड्रोकार्बन की ओर स्थानांतरित कर दिया गया। 10%Fe/20%Co/SiO_2 उत्प्रेरक पर FTS प्रतिक्रिया की kinetics का मानना है कि लैंगमुइर-हिंसहॉलवुड-हौजेन-वॉटसन (L-H-H-W) और एले-रिडेल (E-R) तंत्र का पालन किया। हाइड्रोजन सहायता वाली CO विस्थापन तंत्र के आधार पर CO खपत की दर के लिए विकसित गतिज मॉडल डेटा को पर्याप्त रूप से फिट करते हैं काइनेटिक मॉडल भी उत्पाद निर्माण की दर के लिए विकसित किए गए जिसमें श्रृंखला प्रसार और समापन के तंत्र शामिल किए गए है। चैन लंबाई पर निर्भर मॉडल α-olefin desorption गैर एएसएफ व्यवहार की भविष्यवाणी करने में सक्षम था, मुख्य रूप से पैराफिन अनुपात को कम α-olefin। मीथेन गठन की सक्रियता ऊर्जा (71 kJ/mol) अन्य पैराफिन (113 kJ/mol) से कम थी, जो उत्पाद धारा में मीथेन के मनाया उच्च अंश के साथ समझौता है।

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NOMENCLATURE

E_i	Activation energy for rate constant of reaction i, kJ mol^{-1}
ΔH_i	Heat of adsorption for species i, kJ mol^{-1}
ΔS_i	Entropy of adsorption for species i, J mol^{-1} K^{-1}
K_i	Equilibrium constant of reaction i or adsorption coefficient for surface species i,MPa^{-1}
$r_{i,j}^{exp}$	Experimental rate of formation of component i, mol/gcat-h
$r_{i,j}^{cal}$	Calculated rate of formation of component i, mol/gcat-h
r_{FT}	Rate of Fischer Tropsch reaction, mol/gcat-h
r_{WGS}	Rate of water gas shift reaction, mol/gcat-h
k_i^o	Pre exponential rate constant for reaction i, mol/gcat-h
k_i	Rate constant for reaction i, mol/gcat-h
k_w	Rate constant for water gas shift reaction, mol/gcat-h
P_{H_2}	Partial pressure of H_2, MPa
P_{CO}	Partial pressure of CO, MPa
P_T	Total pressure, MPa
N_{exp}	Total number of experiment
F_{Obj}	Objective function
R^2	Coefficient of correlation
σ	Error variance
*	Vacant active site
α_i	Chain growth probability factor for hydrocarbon with carbon number i

$R_{C_nH_{2n+2}}$	Rate of formation of paraffin with carbon number n
$R_{C_nH_{2n}}$	Rate of formation of olefin with carbon number n
T	Temperature, °C
P	Pressure, MPa
S_g	BET surface area, m^2 $gcat^{-1}$
V_g	Volume of liquid adsorbate, cm^3
d_p	Average pore diameter, m

ACRONYMS

BTL	Biomass to liquid
FTS	Fischer Tropsch Synthesis
WGS	Water gas shift
RWGS	Reverse water gas shift
TEOS	Tetra ethyl ortho-silicate
EtOH	Ethyl Alcohol
LHHW	Langmuir-Hinshelwood- Hougen−Watson
EL	Eley Riedel
atm	atmosphere
BJH	Barrett-Johner-Halenda
BET	Brunauer-Emmett-Teller
DTA	Differential thermal analysis
SEM	SEM scanning electron microscopy
EDX	EDX energy-dispersive X-ray spectroscopy
TEM	TEM transmission electron microscopy
TGA	TGA thermal gravimetric analysis
TPD	TPD temperature programmed desorption
XRD	XRD X-ray diffraction
TPR	TPR temperature programmed reduction
TOF	Turn over frequency
Eq	Equation
BE	Binding energy
ID	Inner diameter
FID	Flame ionization detector
FTIR	Fourier transform infrared spectroscopy

DRIFTS	Diffused reflectance infrared Fourier transform spectroscopy
TCD	Thermal conductivity detector
GHSV	Gas hourly space velocity
JCPDS	Joint committee on powder diffraction standards
MARR	Mean absolute relative residual
RDS	Rate determining step
RMSE	Root mean square error
SCADA	Supervisory control and data acquisition system
Mtoe	Million tonnes of oil equivalent
GHG	Greenhouse gas
CCS	Carbon capture and storage
MMT	Million metric tons