DECOMPOSITION OF SULFUR TRIOXIDE OVER MIXED METAL OXIDE CATALYSTS IN THE SULFUR–IODINE CYCLE FOR HYDROGEN PRODUCTION

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by

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CERTIFICATE

This is to certify that the thesis titled "**Decomposition of Sulfur Trioxide over Mixed Metal Oxide Catalysts in the Sulfur–Iodine Cycle for Hydrogen Production"** being submitted by **Mr. Sachin Tomar** to the Indian Institute of Technology Delhi for the award of Doctor of Philosophy is a record of bonafide research work performed by him under my guidance and supervision in accordance with the rules and regulations of Indian Institute of Technology Delhi.

This thesis contains original work that has not been submitted, in whole or in part, to any other university or institute for the award of a degree or diploma.

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(SACHIN TOMAR)

ABSTRACT

The sulfur–iodine (S–I) cycle is one of the promising thermochemical methods for water–to–hydrogen conversion in an efficient and eco–friendly manner. SO_3 decomposition is the most endothermic reaction of the S–I cycle. Some of the major challenges in the SO_3 decomposition step of the S–I cycle are sintering, long term stability and cost of the catalytic system. Along with the better catalytic design, understanding of the kinetics of the catalytic decomposition is essential for the implementation of the process at a large scale. Reported literature primarily focused on the power–law type models. The literature till date is lacking in the heterogeneous kinetic modeling and validation of the models with the experimental studies of the reaction. Furthermore, separation of the acid mixture ($HI–H_2O–I_2$) is a matter of concern in the S–I process. There is presence of $HI–H_2O–I_2$ (HI_x) phase in sulfuric acid which is the feed for the SO_3 decomposition reaction. The impurities in sulfuric acid have a remarkable influence on the catalytic performance in the SO_3 decomposition reaction. The practical aspect on how the iodine–based impurities could affect catalytic activity has been scarcely addressed until now. From the commercial operation point of view, the severe impact of the feed impurities on the catalytic performance necessitates a highly active and stable catalytic system for SO_3 decomposition in the integrated S–I process.

Hence, there is a need for cost effective, highly active as well as stable catalysts with the right choice of supports in this high temperature endothermic reaction which is important for scale-up of the process. Copper ferrite ($CuFe_2O_4$) was dispersed over the suitable supports and characterized by different physicochemical techniques. The catalysts were activity tested and compared in high temperature (800–900 ˚C) endothermic SO_3 decomposition reaction in the S–I cycle for hydrogen production. The kinetic modeling over the synthesized catalysts was studied. Furthermore, the effect of the feed impurities on the catalytic performance was investigated.

सार

सल्फर-आयोडीन (S–I) चक्र एक कुशल और पर्यावरण के अनुकूल तरीके से जल-से-हाइड्रोजन रूपांतरण के लिए आशाजनक थर्मोकेमिकल विधियों में से एक है। SO_3 अपघटन S–I चक्र की सबसे एंडोथर्मिक प्रतिक्रिया है। S–I चक्र के SO_3 अपघटन चरण में कुछ प्रमुख चुनौतियाँ सिंटरिंग, दीर्घकालिक स्थिरता और उत्प्रेरक प्रणाली की लागत हैं। बेहतर उत्प्रेरक डिजाइन के साथ, बड़े पैमाने पर प्रक्रिया के कार्यान्वयन के लिए उत्प्रेरक अपघटन के कैनेटीक्स की समझ आवश्यक है। रिपोर्टेड साहित्य मुख्य रूप से पावर-लॉ टाइप मॉडल पर केंद्रित है। आज तक के साहित्य में प्रतिक्रिया के प्रायोगिक अध्ययन के साथ विषम काइनेटिक मॉडलिंग और मॉडलों के सत्यापन की कमी है। इसके अलावा, एसिड मिश्रण ($HI–H_2O–I_2$) का पृथक्करण S–I प्रक्रिया में चिंता का विषय है। सल्फ्यूरिक एसिड में $HI–H_2O–I_2$ (HI_x) चरण की उपस्थिति है जो SO_3 अपघटन प्रतिक्रिया के लिए फ़ीड है। सल्फ्यूरिक एसिड में अशुद्धियों का SO_3 अपघटन प्रतिक्रिया में उत्प्रेरक प्रदर्शन पर उल्लेखनीय प्रभाव पड़ता है। आयोडीन-आधारित अशुद्धियाँ उत्प्रेरक गतिविधि को कैसे प्रभावित कर सकती हैं, इस पर व्यावहारिक पहलू को अब तक शायद ही संबोधित किया गया हो। वाणिज्यिक संचालन के दृष्टिकोण से, उत्प्रेरक प्रदर्शन पर फ़ीड अशुद्धियों के गंभीर प्रभाव को एकीकृत एस-आई प्रक्रिया में SO_3 अपघटन के लिए एक अत्यधिक सक्रिय और स्थिर उत्प्रेरक प्रणाली की आवश्यकता होती है।

इसलिए, इस उच्च तापमान एंडोथर्मिक प्रतिक्रिया में समर्थन के सही विकल्प के साथ लागत प्रभावी, अत्यधिक सक्रिय और साथ ही स्थिर उत्प्रेरक की आवश्यकता है जो प्रक्रिया के स्केल-अप के लिए महत्वपूर्ण है। कॉपर फेराइट ($CuFe_2O_4$) को उपयुक्त सपोर्ट पर फैलाया गया और विभिन्न भौतिक-रासायनिक तकनीकों द्वारा विशेषता दी गई। उत्प्रेरकों का गतिविधि परीक्षण किया गया और हाइड्रोजन उत्पादन के लिए S–I चक्र में उच्च तापमान (800–900 °C) एंडोथर्मिक SO_3 अपघटन प्रतिक्रिया की तुलना की गई। संश्लेषित उत्प्रेरकों पर काइनेटिक मॉडलिंग का अध्ययन किया गया। इसके अलावा, उत्प्रेरक प्रदर्शन पर फ़ीड अशुद्धियों के प्रभाव की जांच की गई।

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NOMENCLATURE

Symbols

E_a	Activation energy (kJ/mol)
S_A	BET surface area (m^2/g)
d_p	Crystallite size (nm)
C_{WP}	Weisz–Prater parameter
r_A	Observed rate of reaction (mol/kg_{cat} sec)
R	Radius of the catalyst pellet (m)
D_e	Effective diffusivity (m^2/sec)
C_{AS}	Surface concentration (mol/m^3)
n	Reaction order
k_c	Mass transfer coefficient (m/s)
X	SO_3 conversion
R	Gas constant (J/mol K)
W	Weight of the catalyst (g)
S_F	Exterior surface area per unit volume of reactor bed (Foam) (m^2 $m(bed)^{-3}$)
S_p	Exterior surface area per unit volume of reactor bed (Pellet) (m^2 $m(bed)^{-3}$)
D_p	Pellet diameter (m)
Re_F	Reynold number based on foam catalyst
Re_p	Reynold number based on pellet catalyst
v	Superficial velocity (m/s)
T	Temperature (K)
h_F	Heat transfer coefficient based on foam catalyst (W m^{-2} K^{-1})
h_p	Heat transfer coefficient based on pellet catalyst (W m^{-2} K^{-1})

D	Diameter of the reactor (m)
j_{DF}	Mass transfer factor based on foam catalyst
j_{Dp}	Mass transfer factor based on pellet catalyst
k_F	Mass transfer coefficient based on foam catalyst (m/sec)
k_p	Mass transfer coefficient based on pellet catalyst (m/sec)
Sc	Schmidt number
M_1, M_2	Molecular mass (g/mol)
V_1, V_2	Diffusion volume (cm^3/mol)
ΔP	Pressure drop (Pa)
ρ_c	Density of the catalyst (kg/m^3)
ρ_b	Catalyst bulk density (kg/m^3)
λ	Thermal conductivity ($W\ m^{-1}\ K^{-1}$)
ρ	Density of the gas (kg/m^3)
ε_F	Foam porosity
ε_p	Pellet porosity
μ	Viscosity of the gas ($kg\ m^{-1}\ s^{-1}$)
D_{12}	Diffusivity (m^2/sec)
d_{fp}	Foam pore diameter (m)
d_t	Foam strut diameter (m)
d_F	Mean pore diameter of the foam (m)

Acronyms

S–I	Sulfur–Iodine
XRD	X–ray diffraction
FT–IR	Fourier transform infra–red spectroscopy
TGA	Thermo–gravimetric analysis

XPS	X–ray photoelectron spectroscopy
BET	Brunauer–Emmett–Teller
FESEM–EDS	Field emission scanning electron microscope–energy dispersive X–ray spectroscopy
TEM	Transmission electron microscopy
HR–TEM	High resolution transmission electron microscopy
SAED	Selected area electron diffraction
WHSV	Weight hourly space velocity (h^{-1})
LHHW	Langmuir–Hinshelwood–Hougen–Watson
PPI	Pores per linear inch
RSM	Response surface methodology
DF	Degree of freedom
MS	Mean square
ANOVA	Analysis of variance
SS	Sum of squares