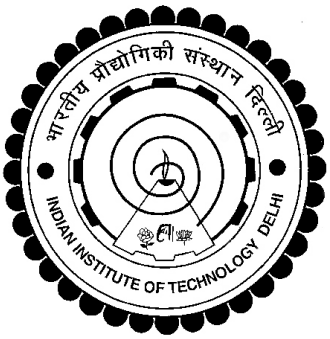
INVESTIGATIONS ON THE CATALYTIC DECOMPOSITION OF SULFURIC ACID IN THE S-I PROCESS FOR HYDROGEN PRODUCTION

K.V. KRISHNA KISHORE



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INVESTIGATIONS ON THE CATALYTIC DECOMPOSITION OF SULFURIC ACID IN THE S-I PROCESS FOR HYDROGEN PRODUCTION

by

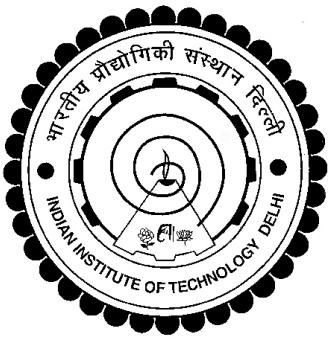
K.V. Krishna Kishore

Chemical Engineering Department

Submitted

In fulfilment of the requirement of the degree of Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

This work is dedicated to my wife Kalpana, and son Dasarha Teja whose sacrifices, which were realized by our loss of precious time together, were for me the most painful and humbling of all.

CERTIFICATE

This is to certify that the thesis entitled, **"Investigations on the catalytic decomposition of sulfuric acid in the S-I process for hydrogen production"** being submitted by **Mr. K.V. Krishna Kishore** to the Indian Institute of Technology Delhi for the award of Doctor of Philosophy is a record of bonafide research work carried out by him under my guidance and supervision in conformity with the rules and regulations of Indian Institute of Technology Delhi.

The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

(Dr. Sreedevi Upadhyayula)

Associate Professor
Department of Chemical Engineering
Indian Institute of Technology Delhi
Hauz Khas, New Delhi-110016

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(K.V. Krishna Kishore)

ABSTRACT

The decomposition of H_2SO_4 to produce SO_2 is the reaction with the highest energy demand in the thermochemical water splitting process in the Sulfur-Iodine (SI) cycle for hydrogen production. It has two challenges, highly corrosive reactants and products, and a large kinetic barrier. The endothermic decomposition of sulfuric acid requires elevated temperatures, greater than 1023 K. Hence, efficient catalysts have to be developed to lower the activation barrier by improving the dissociation efficiency.

In the present work, metal oxides on various supports have been prepared in the laboratory. These catalysts were characterized using XRD, TG-DTA, SEM, BET, TPR and FT-IR. Unique catalyst supports were selected by establishing the best interaction between the catalysts and supports with the help of experimentation, and by theoretical calculation. These prepared catalysts were screened in a fixed bed atmospheric continuous reactor. Detailed kinetics and stability tests (300 hrs. time on stream) were conducted using the most promising catalyst before further scale-up studies.

To scale up any process, reaction kinetics and reactor materials are important. The most corrosion resistant material was selected after performing corrosion studies on different metals at the reaction conditions. A pilot plant for high pressure investigations was designed, fabricated, installed and commissioned using in-house facilities with complete automation. The catalyst turn-over-frequency (TOF) was further tested above atmospheric pressures and was found to reach the highest for this reaction. It is also the most economical, recoverable, environmentally benign catalyst which can withstand high pressures and thermal fluctuations.

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NOMENCLATURE

d	Distance between crystal planes, XRD	(Å)
D	Reactor inner diameter	(mm)
D_p	Pore size (diameter)	(Å)
S_{BET}	BET surface area	(m^2/g)
V	Pore volume	(cm^3/g)
E_a	Apparent energy	(KJ mol^{-1})
k	Specific reaction rate constant	(s^{-1})
k_1	Rate constants of forward reaction	(s^{-1})
T	Temperature	(K)
L	Catalyst bed height	(mm)
N	Number of experimental observation	-
A_0	Apparent Arrhenius frequency factor	(s^{-1})
C_{SO3}	Concentration of SO_3	(kmol rn^{-3})
C_{SO30}	Initial concentration of DIPB	(kmol rn^{-3})
F_{SO3}	Feed flow rate	(kmol h^{-1})
R	Ideal gas law constant (8.314)	(J $mol^{-1}K^{-1}$)
$\Delta H^0_{f(H_2O)}$	Standard enthalpy of formation	(kJ mol^{-1})
$\Delta G^0_{f(H_2O)}$	Gibbs free energy change	(kJ mol^{-1})
TOS	Time on stream	(h)
T_c	Exothermic reaction temperature	(K)
T_h	Endothermic reaction temperature	(K)
W_L	weight loss	(g)
C_r	average corrosion rate	(µm/year)
t_F	time of exposure	(h)
A_F	specimen exposure area	(cm^2)
X_i	Fractional conversion of species i	x_i
M	Atomic weight of the metal	(a.m.u)
W	Mass of catalyst	(g)
i_{corr}	corrosion current density of the material	(A/m^2)
P_A	Partial pressure of gas A	(bar)
P_{H2O}	Partial pressure of H_2O	(bar)
P_{SO3}	Partial pressure of SO_3	(bar)
P_{O2}	Partial pressure of O_2	(bar)
P_{N2}	Partial pressure of N_2	(bar)
q_r	Heat flux	w/cm^2
W_{SO3r}	Flux of SO_3	-

k_m	Mass transfer coefficient	m/s
K	Equilibrium constant	-

Greek letters

λ	X-ray wavelength	(Å)
φ	Constant in XRD	-
ϕ	Thiele modulus	-
η	Effectiveness factor	-
θ	Diffraction angle	-
Θ_s	Fraction of the vacant catalytic sites	-
β	Peak width at half height	-
υ	Wave number	(cm^{-1})
τ	Space time	(h^{-1}/s^{-1})
ρ	density of the material	(g/cm^3)
μ	viscosity	($g\ cm^{-1}\ s^{-1}$)

Subscripts

i	Reaction or product species

Acronyms

atm	Atmosphere
BJH	Barrett-Johner-Halenda
BET	Brunauer-Emmett-Teller
SI	Sulphur iodine
ID	Inner diameter
FTIR	Fourier transform infrared spectroscopy
WHSV	Weight hour space velocity
GHSV	Gas hourly space velocity
HRTEM	High resolution transmission electron microscopy
JCPDS	Joint committee on powder diffraction standards
LH	Langmuir-Hinshelwood
MFC	Mass flow controller
PID	Proportional-integral-derivative
SCADA	Supervisory control and data acquisition
SiSiC	Silicated Silicon Carbide

SEM	Scanning electron microscopy
STP	Standard temperature and pressure
TCD	Thermal conductivity detector
RSM	Response surface methodology
GC	Gas chromatography
TEM	Transmission electron microscopy
TGA	Thermal gravimetric analysis
TPR	Temperature programmed reduction
W/F	Weight of catalyst/molar flow rate of methane
WI	Wet impregnation
TOF	Catalyst turn over frequency
XRD	X-ray diffraction